

MICROBIOLOGICAL CONTROL IN AQUEOUS SYSTEMS**REFERENCE TO RELATED APPLICATIONS**

This Application is a continuation-in-part of commonly-owned copending Application Nos. 09/484,938, filed January 18, 2000 and __[Case No. SU-7190]__ filed February 2, 2001.

REFERENCE TO OTHER COMMONLY-OWNED APPLICATIONS

5 Commonly-owned copending Application No. 09/484,844, filed January 18, 2000, describes and claims chemical processes from which compositions of the present invention can be formed or derived. Commonly-owned copending Application No. 09/484,687, filed January 18, 2000, describes and claims 1,3-dibromo-5,5-dimethylhydantoin particulate solids producible by the processes of Application No. 09/484,844, such solids having enhanced properties, and compacted articles made from such particulate solids without use of a binder. Commonly-owned copending Application No. 09/487,816, filed January 18, 2000, relates in part to converting 1,3-dihalo-5,5-dimethylhydantoins into compacted articles using novel binders. Commonly-owned copending Application No. 09/484,891, filed January 18, 2000, relates to the compacting of 1,3-dihalo-5,5-dimethylhydantoins other than 1,3-dibromo-5,5-dimethylhydantoin without use of binders, and to the novel compacted forms so produced. Commonly-owned copending Application No. 09/483,896, filed January 18, 2000, relates to the granulation of small average particle size 1,3-dibromo-5,5-dimethylhydantoin and also to the compaction of such granulated products to form larger-sized articles.

BACKGROUND

20 Persons using biocidal agents in the biocidal treatment of water customarily, if not universally, refer to "free chlorine" level as a measure of biocidal control. To achieve "free chlorine" levels in water treatment, solid materials are often preferred because of their high weight percent activity. N,N'-bromochloro-5,5-dimethylhydantion (BCDMH) has been one of the most widely-used solid sources of "free chlorine" for water treatment. One of the features emphasized for BCDMH by suppliers of BCDMH is that in use, the combined chlorine from the biocide regenerates "free chlorine" by reaction with inactive bromide

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species formed during the water treatment operation. In other words, the chlorine atom in the initial N,N'-bromochloro-5,5-dialkylhydantoin is said to be a precursor for additional "free chlorine" for sanitation purposes.

5 In use, BCDMH hydrolyzes into HOBr and HOCl both of which register as "free chlorine" species in commonly-used standard test procedures. These methods for determining "free chlorine" levels in treated water, involve use of a reagent known as DPD (*i.e.*, N,N'-diethyldiphenylenediamine) and a buffer, and the results of such analyses are commonly used, if not universally used, as the basis for determining the quantity of a halogen-containing microbiocidal agent to be used for water treatment. Heretofore, consumers of BCDMH have only been concerned with the level of "free chlorine" provided by a given quantity of that biocidal material. What has not been realized by such consumers is the amount of "total chlorine" being utilized in order to achieve the requisite "free chlorine" level. As a consequence, the consumer has not had available a yardstick by which to determine the true economic efficiency of using BCDMH as a biocidal agent in the treatment of water. To achieve optimum economic efficiency, the consumer should have available for use a biocidal agent in which the amount of "free chlorine" released into the water corresponds closely to the "total chlorine" content of the biocidal agent.

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25 In the event a biocidal agent provides a relatively small amount of "free chlorine" in relation to its "total chlorine" content, it has been deemed necessary to utilize a relatively large amount of such agent in order to achieve microbiological control. This in turn means high levels of halogenated materials are released into the environment. If on the other hand, a biocidal agent could provide to the water an amount of "free chlorine" that closely corresponds to the "total chlorine" content of the biocidal agent, effective microbiological control could be realized by use of much smaller dosages and with consequent minimal adverse impact upon the environment.

Another serious problem in connection with water disinfection is biofilm development. Biofilms are bacterial films which tenaciously adhere to surfaces in contact with water such as heat exchanger surfaces, conduit interiors, filters, and other processing equipment. These films are very undesirable because they can harbor dangerous pathogens, and cause damage to the surfaces to which they have become attached. Moreover, the bacteria form a slime layer of extra-cellular polysaccharide which affords protection to the bacteria and in addition constitute an effective barrier against penetration of biocidal agents used in an attempt to combat such bacteria. In situations where the water is prone to development of calcium carbonate scale, the presence of such gelatinous extra-cellular polysaccharides can result in the formation of layers of scale bonded to the substrate surface by the gelatinous polysaccharides. Polysaccharide films and films of scale bonded by means of polysaccharides can greatly interfere with the operation of heat exchangers by virtue of their insulating characteristics, and can markedly interfere with the functioning of filters and the flow of water through pipes and conduits by virtue of the clogging tendencies of such polysaccharide films.

Thus a need exists for a biocidal agent which is highly effective in providing biocidal control, especially eradication, or at least minimization, of biofilms in water systems, and in addition, a biocidal agent which has the capability of providing such biocidal control even though used at very low concentrations in water. In addition, a need exists for a biocidal agent that can provide to the water an amount of "free chlorine" that closely corresponds to the "total chlorine" content of the biocidal agent, whereby effective microbiological control can be realized by use of smaller dosages and with consequent minimal adverse impact upon the environment.

SUMMARY OF THE INVENTION

This invention fulfills the foregoing needs in a highly efficient and effective manner.

In accordance with this invention the foregoing needs are fulfilled by the provision of two different categories of biocidally-active 1,3-dibromo-5,5-dialkylhydantoin biocidal

compositions in readily identifiable forms. In one such category the only biocidally-active component of the biocidal composition is at least one 1,3-dibromo-5,5-dialkylhydantoin in which one of the alkyl groups in the 5-position is a methyl group and the other alkyl group in the 5-position contains in the range of 1 to 4 carbon atoms (DBDAH). In the other such category the biocidally-active components of the biocidal composition are a combination of (i) DBDAH and (ii) at least one non-fluid biocidally-active water treating agent compatible with DBDAH, wherein the weight ratio of (i) to (ii) is in the range of 0.1:0.4 to 99.9:0.1, preferably in the range of 1:1 to 99.9:0.1, more preferably in the range of 9:1 to 99.9:0.1, and most preferably in the range of 19:1 to 99.9:0.1. Each such category of biocidally-active component or components can be in admixture with from 0 to 90 wt% of biocidally-inactive components such as for example one or more binders, fillers, excipients, dyes or colorants, perfumes, stabilizers, and/or manufacturing by-products. In these biocidal compositions the balance, if any, to 100 wt% of the compositions is one or more biocidally-inactive materials.

Pursuant to one embodiment of this invention, such biocidal compositions are provided for use as a biocide or disinfectant in aqueous systems such as wastewater, commercial and industrial recirculating cooling water systems, industrial once-through cooling water systems, brewery pasteurizers, recreational water (swimming pools, hot tubs, and spas), pulp and paper mill systems, air washer systems, air and gas scrubber systems, decorative fountains, and hard surface sanitizers. In another embodiment such biocidal compositions are provided for use in the formulation of fungicides, algicides, slimicides, and microbiocides for use in such aqueous systems.

Of the above two categories of biocidal compositions, the preferred category is the one in which the only biocidally-active component of the biocidal composition is at least one 1,3-dibromo-5,5-dialkylhydantoin in which one of the alkyl groups in the 5-position is a methyl group and the other alkyl group in the 5-position contains in the range of 1 to 4 carbon atoms (DBDAH).

As will be seen hereinafter, a biocide or disinfectant of this invention has been found to be much more effective than the prior commercial standard in the art, the ubiquitous N,N'-bromochloro-5,5-dimethylhydantoin, in providing microbiological control against various undesirable microbial species. Moreover, it has been found that there is a substantial disparity between the "free chlorine" level and the "total chlorine" level delivered to the water when using N,N'-bromochloro-5,5-dimethylhydantoin (BCDMH) as a biocidal agent. Thus the consumer of BCDMH as a water treating agent unknowingly has been paying for a relatively ineffective microbiocidal agent. Moreover, such consumer has been contributing unknowingly to the release of undesirable quantities of halogenated materials to the environment. In sharp contrast, the level of "free chlorine" in water available from 1,3-dibromo-5,5-dimethylhydantoin (DBDMH) closely approximates its "total chlorine" content thus eliminating these adverse consequences associated with the purchase and use of BCDMH as a water treating agent.

Thus, in accordance with one embodiment of this invention, there is provided an article of manufacture comprising a packaging material and a biocidal composition contained within said packaging material, wherein said biocidal composition is a biocidal composition described above, and wherein said packaging material comprises at least a label suitably identifying the name of the product in the package, and at least a sticker identifying the contents as being an oxidizing agent. Preferably the foregoing label or another label associated with the packaging material will indicate the hazards associated with the handling and use of the packaged composition, and if such article of manufacture is to be exported from one country to another, it is particularly preferred that such precautionary statements relating to such hazards be written in the language of the recipient country. More preferably, the foregoing label or another label associated with the packaging material will indicate that an active ingredient of the composition contained within said packaging material is the one or more of the above-specified 1,3-dibromo-5,5-dialkylhydantoins actually contained therein. Still more preferably, the actual proportion or percentage (typically in terms of wt%) of such one or more 1,3-dibromo-5,5-dialkylhydantoins in the packaged composition will be specified

or at least indicated on such label. Even more preferably, such labeling will indicate the actual proportion or percentage (typically in terms of wt%) of inactive contents in the composition contained within said packaging material.

In accordance with other preferred embodiments of this invention, there is provided an article of manufacture as described above wherein said packaging material comprises a label that, *inter alia*, identifies the product by name, indicates its function(s) uses or use patterns, and identifies as an active ingredient of the composition contained within said packaging material, the one or more such 1,3-dibromo-5,5-dialkylhydantoins actually contained therein. If such packaged biocidal composition includes one or more additional biocidally-active ingredients compatible with such one or more 1,3-dibromo-5,5-dialkylhydantoins, the label will identify as an active ingredient of the composition contained within said packaging material, each of the one or more such additional biocidally-active ingredients actually contained therein. More preferably, the foregoing label will additionally set forth at least one or more (and most preferably all) of the following:

- a) the identity of each other active ingredient of said composition, if there is any such other active ingredient present in the composition;
- b) the amount (typically in terms of wt%) of each active ingredient present in the composition;
- c) precautionary statements relating to hazards to humans and domestic animals associated with the handling and use of the composition;
- d) description of environmental hazards associated with discharge of the composition into the environment;
- e) description of physical and chemical hazards, and indications of how to avoid or at least reduce such hazards in use;
- f) advice on storage of the product, and on disposal of the product and containers;
- g) advice concerning practical treatment and first aid to be used in the event of contact of the composition with eyes or skin, or if the composition is ingested (swallowed) or inhaled;

- h) directions for use, including but not limited to dosage rates associated with specified use patterns; and
- i) EPA registration number, EPA establishment number, and name and address of the registrant (*i.e.*, the registration holder).

5 This invention provides in another of its embodiments an article of manufacture capable of providing to the purchaser or user thereof (A) microbiological control in an aqueous medium such as wastewater, recirculating cooling water systems, once-through cooling water systems, brewery pasteurizers, recreational water, pulp and paper mill systems, air washer systems, air and gas scrubber systems, decorative fountains, or any combination of any two or more of these, wherein the recreational water referred to comprises one or more of swimming pools, hot tubs, and spas, and/or (B) eradication or reduction of biofilm on a surface in contact with such aqueous medium. This article of manufacture comprises a packaging material and a biocidal composition contained within said packaging material. The biocidally-active ingredient of such composition is at least one 1,3-dibromo-5,5-dialkylhydantoin in which one of the alkyl groups in the 5-position is a methyl group and the other alkyl group in the 5-position contains in the range of 1 to 4 carbon atoms (DBDAH). The packaging material comprises a label that indicates that the product can be used as a biocidal agent or disinfectant for water treatment and contains recommended dosage rates for use or use patterns (types of systems to be treated), whereby in use (i) the molar quantity of the DBDAH introduced into the water can be less than the molar quantity of N,N'-bromochloro-5,5-dimethylhydantoin (BCDMH) that would be required to effect the same degree of microbiological control in such medium, (ii) the quantity of DBDAH introduced into such aqueous medium releases an amount of "free chlorine" that is greater than the amount of "free chlorine" that would be released in such medium by an equimolar quantity of BCDMH, and (iii) the amount of "free chlorine" released by the quantity of such at least one DBDAH introduced into such aqueous medium is greater than the amount of "free chlorine" that could be predicted to be released by that quantity of DBDAH on the basis of the amount of "free chlorine" that would be released in such medium by an equimolar quantity of BCDMH. The

most preferred DBDAH used in this embodiment is 1,3-dibromo-5,5-dimethylhydantoin (DBDMH).

In one particularly preferred embodiment of this invention, there is provided an article of manufacture comprising a packaging material and a biocidal composition contained within said packaging material, wherein said biocidal composition comprises as an active ingredient(s) of the composition at least at least 95 wt%, more preferably at least 97 wt%, and most preferably at least 99 wt%, of one or more 1,3-dibromo-5,5-dialkylhydantoins in which one of the alkyl groups in the 5-position is a methyl group and in which the other alkyl group in the 5-position has in the range of 1 to 4 carbon atoms, most preferably 1,3-dibromo-5,5-dimethylhydantoin, with the balance, if any, to 100 wt% being inactive ingredient(s), wherein said packaging material comprises a label that indicates that the product can be used as a biocide for wastewater, recirculating cooling water systems, once-through cooling water systems, brewery pasteurizers, pulp and paper mill systems, air washer systems, air and gas scrubber systems, or decorative fountains, or any combination of any two or more of these. In addition it is preferred that the label indicate that the product can be used as a biocide for at least four (4) of the foregoing eight (8) uses or use patterns, and most preferably for all eight (8) of the foregoing eight (8) uses or use patterns. It is further preferred that such label indicate that the dosage rate for at least one (1) and more preferably at least four (4) of the foregoing eight (8) uses or use patterns be such as to maintain a residual bromine level of 0.5-5 ppm or as needed to maintain control.

In another particularly preferred embodiment of this invention, there is provided an article of manufacture comprising a packaging material and a biocidal composition contained within said packaging material, wherein said biocidal composition comprises as an active ingredient of the composition at least 95 wt%, more preferably at least 97 wt%, and most preferably at least 99 wt%, of one or more 1,3-dibromo-5,5-dialkylhydantoins in which one of the alkyl groups in the 5-position is a methyl group and in which the other alkyl group in the 5-position has in the range of 1 to 4 carbon atoms, most preferably 1,3-dibromo-5,5-

dimethylhydantoin, with the balance, if any, to 100 wt% being inactive ingredient(s), wherein said packaging material comprises a label that indicates that the product can be used by manufacturers in formulating biocides for wastewater, recirculating cooling water systems, once-through cooling water systems, brewery pasteurizers, recreational water, pulp and paper mill systems, air washer systems, air and gas scrubber systems, decorative fountains, or hard surface sanitizers, or any combination of any two or more of these, wherein the recreational water referred to comprises one or more of swimming pools, hot tubs, and spas. In addition it is preferred that the label indicate that formulators using the product are responsible for EPA registration of their formulated products.

In still another particularly preferred embodiment of this invention, there is provided an article of manufacture comprising a packaging material and a biocidal composition contained within said packaging material, wherein said biocidal composition comprises as an active ingredient of the composition at least at least 95 wt%, more preferably at least 97 wt%, and most preferably at least 99 wt%, of one or more 1,3-dibromo-5,5-dialkylhydantoins in which one of the alkyl groups in the 5-position is a methyl group and in which the other alkyl group in the 5-position has in the range of 1 to 4 carbon atoms, most preferably 1,3-dibromo-5,5-dimethylhydantoin, with the balance, if any, to 100 wt% being inactive ingredient(s), wherein said packaging material comprises a label that indicates that the product can be used as a biocidal agent or disinfectant for use in pools, spas, and/or hot tubs. It is further preferred that such label indicate that:

- 1) the level of active bromine be maintained between 2-4 ppm in residential spas or hot tubs and 3-6 ppm in commercial spas or hot tubs with the pH of the water being adjusted to 7.2-7.6 prior to initiating treatment with the biocidal composition; and/or
- 2) the level of active bromine be maintained between 1-4 ppm in swimming pools with the pH of the water being adjusted to 7.2-7.6 prior to initiating treatment with the biocidal composition.

Another embodiment of this invention is the method of purveying a microbiological control agent for water, which method comprises purveying an article of manufacture of this invention as described herein.

Yet another embodiment of this invention is the method of purveying a microbiological control agent for water in accordance with U.S. Environmental Protection Agency regulations, which method comprises purveying a container of a water control agent comprising as an active ingredient at least 20 wt%, preferably at least 50 wt%, more preferably at least 90 wt%, and most preferably at least 95 wt% of one or more 1,3-dibromo-5,5-dialkylhydantoin in which one of the alkyl groups in the 5-position is a methyl group and the other alkyl group in the 5-position contains in the range of 1 to 4 carbon atoms, said container bearing an official sticker identifying the contents as being an oxidizing agent, and a label having thereon dosage levels and all information required pursuant to requirements promulgated by the U.S. Environmental Protection Agency.

Typically, the biocidal compositions or water control agents provided pursuant to this invention will be in powder form, or in a compacted form, such as granules, nuggets, pellets, tablets, briquettes, or pucks.

Other embodiments, features, and advantages of this invention will be still further apparent from the ensuing description and appended claims.

BRIEF DESCRIPTION OF THE DRAWING

Fig. 1 is a graphical representation of the results of standard "free chlorine" and "total chlorine" tests performed on simulated cooling water solutions dosed with BCDMH or DBDMH, all as described in detail in Example 1 hereinafter.

Fig. 2 is a graphical representation of the percent of hydrolysis experienced by the respective test samples of BCDMH and of DBDMH in the tests performed in Example 1.

FURTHER DETAILED DESCRIPTION

Heretofore the art has regarded BCDMH as being a biocidal agent of choice because of the levels of effectiveness achieved by use of that agent. Moreover, it is surprising that in an aqueous medium the amount of "free chlorine" released by a DBDAH such as DBDMH is greater than the amount of "free chlorine" released by an equimolar quantity of BCDMH. At best the expectation would be that there could be no significant difference, and thus that there would be no appreciable difference, in these respective amounts of "free chlorine". Furthermore, not until comparative testing of water samples with a pH of greater than about 8.0 containing, respectively, equimolar quantities of DBDMH or BCDMH for "free chlorine" using Hach Method 8021 (copyright 1997, by Hach Company) and for "total chlorine" using Hach Method 8167 (copyright 1997, by Hach Company), and converting the mg/L Cl₂ "free chlorine" values from the tests to percentages of the mg/L Cl₂ "total chlorine" values from the tests, was the unpredictable superiority of DBDMH in releasing larger amounts of "free chlorine" than the equimolar quantity of BCDMH discovered. Prior to such testing there was no way of predicting the existence this superiority.

As a consequence of the above surprising features of this invention it is now possible to achieve the same microbiocidal effect on or control of bacteria, algae, biofilm, and like microbiological entities as given by BCDMH but using smaller molar amounts of one or more of the above described 1,3-dibromo-5,5-dialkylhydantoins such as DBDMH, and at the same time significantly reducing the amounts of halogenated materials to be released to the environment. Alternatively, greater microbiocidal control of bacteria, algae, biofilm, and like microbiological entities can be achieved using one or more of the above described 1,3-dibromo-5,5-dialkylhydantoins such as DBDMH in the same molar quantity as BCDMH, or even somewhat less molar quantity of one or more such 1,3-dibromo-5,5-dialkylhydantoins than BCDMH.

Because of such surprising discoveries, it is now possible to provide as one category of biocidally-active compositions a biocide or disinfectant in which at least 20 wt%,

preferably at least 50 wt%, more preferably at least 90 wt%, and most preferably at least 95 wt% of the biocide or disinfectant composition is one or a mixture of such 1,3-dibromo-5,5-dialkylhydantoins (DBDAH). The balance, if any, to 100 wt% is made up of one or more biocidally-inactive ingredients, such as for example one or more binders, fillers, excipients, dyes or colorants, perfumes, stabilizers, and/or manufacturing by-products.

Thus articles of manufacture as described above in which are packaged biocidal or disinfectant compositions consisting essentially of one or a mixture of the above-described 1,3-dibromo-5,5-dialkylhydantoins (DBDAH) identified on a label affixed to or held in contact with the package and visible from the exterior of the package, as the active ingredient(s) are provided by this invention. Likewise this invention provides articles of manufacture as described above in which are packaged biocidal or disinfectant compositions consisting essentially of (i) 20 to 99.9 wt% of one or a mixture of such 1,3-dibromo-5,5-dialkylhydantoins (DBDAH) identified on a label affixed to or held in contact with the package and visible from the exterior of the package, as the active ingredient(s) together with (ii) 0.1 to 80 wt% of one or more biocidally-inactive ingredients, the total of (i) and (ii) being 100 wt%.

The 1,3-dibromo-5,5-dialkylhydantoins utilized in the practice of this invention are those in which one of the alkyl groups in the 5-position is a methyl group and the other alkyl group in the 5-position is an alkyl group having in the range of 1 to 4 carbon atoms. Thus the biocides used in this invention comprise 1,3-dibromo-5,5-dimethylhydantoin, 1,3-dibromo-5-ethyl-5-methylhydantoin, 1,3-dibromo-5-n-propyl-5-methylhydantoin, 1,3-dibromo-5-isopropyl-5-methylhydantoin, 1,3-dibromo-5-n-butyl-5-methylhydantoin, 1,3-dibromo-5-isobutyl-5-methylhydantoin, 1,3-dibromo-5-sec-butyl-5-methylhydantoin, 1,3-dibromo-5-tert-butyl-5-methylhydantoin, and mixtures of any two or more of them. Such compounds have sufficient water solubility for use in water treatment. Of these biocidal agents, 1,3-dibromo-5-isobutyl-5-methylhydantoin, 1,3-dibromo-5-n-propyl-5-methylhydantoin, and 1,3-dibromo-5-ethyl-5-methylhydantoin are, respectively, preferred, more preferred, and even more preferred

members of this group from the cost effectiveness standpoint. Of the mixtures of the foregoing biocides that can be used pursuant to this invention, it is preferred to use 1,3-dibromo-5,5-dimethylhydantoin as one of the components, with a mixture of 1,3-dibromo-5,5-dimethylhydantoin and 1,3-dibromo-5-ethyl-5-methylhydantoin being particularly preferred.

5 The most preferred biocide employed in the practice of this invention is 1,3-dibromo-5,5-dimethylhydantoin.

When a mixture of two or more of the foregoing biocides is made up or used pursuant to this invention, the individual biocides of the mixture can be in any proportions relative to each other.

As noted above, the biocidally-inactive ingredient(s) may include for example one or more binders, fillers, excipients, dyes or colorants, stabilizers, perfumes, and/or manufacturing by-products. Most of these inactive ingredients are conventional, and are well-known to those of ordinary skill in the art. Such inactive ingredients to the extent present in detectable quantities are disclosed to the U.S. Environmental Protection Agency in terms of their chemical composition in a confidential disclosure form. Such ingredients are typically referred to on the label as "other" ingredients, "inert" ingredients, "inactive" ingredients or by a use of a term of similar import. A preferred type of binder for producing compacted products is a saturated, normally solid, fatty amide as described in U.S. Pat. No. 5,565,576, issued October 15, 1996 to L. K. Hall, J. A. Falter, and T. E. Farina, the disclosure of which

10 patent is incorporated herein *in toto* as if fully set forth herein. A particularly preferred type of binder for use in producing the compacted forms of DBDAH in the practice of this invention is a micronized synthetic polyolefin-based hydrocarbon wax and/or a micronized synthetic polyfluorocarbon wax effective to form the compacted product, provided the wax is suitably compatible with the DBDAH. In the practice of this invention with compacted

15 forms of blends of 1,3-dibromo-5,5-dimethylhydantoin with a micronized synthetic polyolefin-based hydrocarbon wax and/or a micronized synthetic polyfluorocarbon wax, the average particle size of the 1,3-dibromo-5,5-dimethylhydantoin can be in the range of about

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20 to about 600 microns, but preferably the average particle size of the 1,3-dibromo-5,5-dimethylhydantoin is in the range of about 175 to about 400 microns, if not even greater.

Also because of the surprisingly great effectiveness of one or a mixture of 1,3-dibromo-5,5-dialkylhydantoins in which one of the alkyl groups in the 5-position is a methyl group and in which the other alkyl group in the 5-position contains in the range of 1 to 4 carbon atoms (hereinafter sometimes referred to as "DBDAH"), it is now possible to provide as another category of biocidally-active compositions a biocide or disinfectant in which the biocidally-active components of the biocidal composition are a combination of (a) DBDAH and (b) at least one non-fluid biocidally-active water treating agent compatible with DBDAH, wherein the weight ratio of (a) to (b) is in the range of 0.1:0.4 to 99.9:0.1, preferably in the range of 1:1 to 99.9:0.1, more preferably in the range of 9:1 to 99.9:0.1, and most preferably in the range of 19:1 to 99.9:0.1. Such combination of biocidally-active components can be in admixture with from 0 to 90 wt% of biocidally-inactive components such as for example one or more binders, fillers, excipients, dyes or colorants, perfumes, stabilizers, and/or manufacturing by-products. Thus the overall biocidal composition of this category can contain (a) 20 to 99.9 wt% of DBDAH, (b) 0.1 to 80 wt% of one or more non-fluid biocidally-active water treating agents compatible with the DBDAH in the composition, and (c) 0 to 90 wt% of one or more biocidally-inactive ingredients, the total of (a), (b), and (c) being 100 wt%.

Accordingly, this invention also provides articles of manufacture as described above in which are packaged biocidal or disinfectant compositions consisting essentially of (a) 20 to 99.9 wt% of DBDAH identified on a label affixed to or held in contact with the package and visible from the exterior of the package, as active ingredient(s), (b) 0.1 to 80 wt% of one or more other non-fluid biocidally-active water treating agents compatible with the DBDAH in the composition and identified on a label affixed to or held in contact with the package and visible from the exterior of the package, as active ingredient(s), and (c) 0 to 90 wt% of one or more biocidally-inactive ingredients, the total wt% of (a), (b), and (c) being 100 wt%.

Ingredients (a) (*i.e.*, DBDAH) and (c) (*i.e.*, inactive ingredients) have been described above. The one or more other non-fluid biocidally-active water treating agents compatible with the DBDAH utilized as ingredient(s) (b) above are preferably other biocidally-active water-soluble 1,3-dihalo-5,5-dialkylhydantoin, such as 1,3-dichloro-5,5-dimethylhydantoin, 1,3-dichloro-5-ethyl-5-methylhydantoin, 1,3-dichloro-5-n-propyl-5-methylhydantoin, 1,3-dichloro-5-isopropyl-5-methylhydantoin, 1,3-dichloro-5-n-butyl-5-methylhydantoin, 1,3-dichloro-5-isobutyl-5-methylhydantoin, 1,3-dichloro-5-sec-butyl-5-methylhydantoin, 1,3-dichloro-5-tert-butyl-5-methylhydantoin, and mixtures of any two or more of them. Less desirable, but usable, are such compounds as N,N'-bromochloro-5,5-dimethylhydantoin, N,N'-bromochloro-5-ethyl-5-methylhydantoin, 1-bromo-5,5-dimethylhydantoin, 3-bromo-5,5-dimethylhydantoin, 1-chloro-5,5-dimethylhydantoin, 3-chloro-5,5-dimethylhydantoin, and their water-soluble homologs. Non-limiting examples of other biocides that may be used include sodium dichloroisocyanurate, trichloroisocyanuric acid, calcium hypochlorite, and lithium hypochlorite. In order to reduce odor and increase compatibility with DBDAH, it is possible to encapsulate with a water-soluble film, some types of non-fluid biocidally-active water treating agents that can be used with DBDAH.

Naturally all applicable laws, rules, and regulations of the country or countries in which the article of manufacture of this invention is manufactured, sold, transported, and used need to be complied with, including all matters pertaining to the labeling on the article of manufacture.

In certain embodiments of this invention the packaging material comprises a label that indicates, denotes, designates, signifies, or specifies that an active ingredient of the composition is one or more such 1,3-dibromo-5,5-dialkylhydantoin (DBDAH). In addition, such label will indicate, denote, designate, signify or specify the percentage of the DBDAH actually present in the composition, such percentage being at least 20 wt%, preferably at least 50 wt%, more preferably at least 90 wt%, and most preferably in the range of 95 to 100 wt% of the total ingredients of the biocide or disinfectant composition.

5 The packaging material itself can comprise glass, plastic, metal, cardboard, or any other suitable inert material, or any combination of materials, that does not react with any of the ingredients therein. The packaging material serves as one or more containers for the biocidal composition, and may itself define an enclosure in which at least a portion of the interior walls is in direct contact with the ingredients therein, such as for example, a box, drum, pail, can, bag, jar or similar container. Such interior walls may have, and if the container is a metal container should have, a protective coating or liner thereon. Alternatively, the packaging material may comprise an exterior portion serving as housing for one or more internal containers encased within the exterior portion, such as for example a box, crate, bag, drum, or jar within which is disposed at least one internal container. For example the packaging material can be an outer container such as a box or pail containing one or more bags or boxes in which the ingredients are disposed. Other similar packaging materials may occur to those of ordinary skill in the art after a reading of this disclosure.

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20 The packaging material preferably also comprises one or more entrance sites enabling the contents of the package to be withdrawn, for example either (i) directly as all or a portion of the ingredients (*e.g.*, by pouring, scooping, unwrapping, or otherwise extracting or recovering ingredients from the package), or (ii) indirectly as one or more intact smaller packages, which smaller packages in turn are opened as needed to gain access to the ingredients. These and perhaps other ways of providing access to the ingredients will, after reading this disclosure, be readily apparent to those of ordinary skill in the art.

25 Typically, the label is suitably affixed to the exterior of the packaging material. However, a transparent (or slightly translucent) overwrap may be applied to the package or packages over the label so that the label can be read without removing the overwrap. For example, a plurality of unlabeled containers can be disposed on a pallet with a transparent overwrap affixed to the upper portion of the pallet and encasing the containers. In such a package, a label can be disposed within the overwrap at a site which can be viewed from the

exterior. Similarly, the package can be a rigid or semi-rigid container encased by transparent shrink film which also encases the label so that it can be viewed from the exterior.

Preferably the label is adhesively attached to the exterior of the packaging material, as for example by use of a printed paper label with a suitable adhesive substance on its reverse side. Alternatively, the label may be imprinted directly onto the exterior surface of the packaging material, for example by use of a screen printing process. Any other suitable way of labeling the packing material, *e.g.*, stenciling, may be used, if desired.

Preferably, the label of the articles of manufacture of this invention will identify the active ingredient(s) of the composition contained within the package, at least one of which must be DBDAH. In addition, the preferred labels will specify the amount (typically in terms of wt%) of each active ingredient present in the composition contained within the package, as well as the amount (typically in terms of wt%) of any inactive ingredient(s) present in the composition contained within the package. In more preferred articles of manufacture of this invention, the label will also contain dosage rate information. In each embodiment of this invention it is desirable, if not required, to include a visible sticker indicating that the contents of the package constitute an oxidizing agent.

As regards the unprecedented, highly advantageous, features of this invention, it should be understood to begin with that the terms "free chlorine" and "total chlorine" are terms commonly used by persons in the fields of industrial and recreational water treatment. The values for the levels of "free chlorine" and "total chlorine" in the water are determined by use of appropriate standard test procedures which differentiate between the two. Further, the terms "free chlorine" and "total chlorine" are not restricted to just chlorine species in the water but rather, include certain bromine species in the water as well. Thus in a case where a biocidal agent used in treating the water contains both bromine and chlorine atoms (*e.g.*, N,N'-bromochloro-5,5-dimethylhydantoin (BCDMH)), the "free chlorine" and "total chlorine" levels determined in the respective appropriate test procedures used would include

quantification of the sum of the bromine species and chlorine species present that respond to the respective tests. The sum of these respective levels is reported, however, as "free chlorine" or "total chlorine", depending on the test used. Similarly, if the water treating agent used contains bromine atoms but no chlorine atoms, the "free chlorine" and "total chlorine" levels determined in the respective appropriate standard test procedures used would involve quantification of the level of bromine species present that respond to the respective tests. Thus although the halogen species actually present in such case are bromine-containing species, the levels present as determined in the respective tests would be reported as "free chlorine" and "total chlorine", respectively.

Heretofore it has been universally believed that all bromine species dissolved in the water respond positively in the standard "free chlorine" test procedure. However, one of the features of this invention is the discovery that this universal belief is erroneous when the "free chlorine" test procedure is applied to recreational water, cooling water, process water, wastewater or the like, that contains bromine species, and especially to cooling water, process water, and wastewater that is has a pH above about 8.0. Under these conditions the dibromo-containing microbiocides used pursuant to this invention can give vastly superior values for "free chlorine" as compared to the corresponding bromochloro microbiocides as evidenced by the results described herein in which comparisons were made between DBDMH and BCDMH.

For example, it has been found that when water having a pH above about 8.0 is treated with BCDMH to reach a desired "free chlorine" level, the amount of BCDMH being used is far greater than necessary to achieve a given level of microbiocidal effectiveness. This in turn means that the consumer has purchased and is using much more of the microbiocidal agent than necessary. As a consequence, there are involved both an economic penalty due to excessive consumption, and an environmental penalty due to release of excessive quantities of less biocidally-active halogen species to the environment.

Nevertheless, the "free chlorine" level in water treated with a halogen-releasing biocidal agent remains the yardstick by which microbiocidal performance is measured. Species which respond to the standard "free chlorine" test are HOCl and HOBr. Any other form of soluble halogen species do not respond to the standard "free chlorine" test. Such non-responsive species include, for example, chlorine species bound to a nitrogen atom. On the other hand, the standard "total chlorine" test measures both HOBr and HOCl, and any halogen species that do not respond to the standard "free chlorine " test.

The standard tests for determination of "free chlorine" and "total chlorine" are based on classical test procedures devised by Palin in 1974. See A. T. Palin, "Analytical Control of Water Disinfection With Special Reference to Differential DPD Methods For Chlorine, Chlorine Dioxide, Bromine, Iodine and Ozone", *J. Inst. Water Eng.*, 1974, 28, 139. While there are various modernized versions of the Palin procedures, the version of the tests for "free chlorine" and "total chlorine" used and to be used as the standard in connection with this invention, are fully described in *Hach Water Analysis Handbook*, 3rd edition, copyright 1997. The procedure for "free chlorine" is identified in that publication as Method 8021 appearing on page 335, whereas the procedure for "total chlorine" is Method 8167 appearing at page 379. Briefly, the "free chlorine" test involves introducing to the halogenated water a powder comprising DPD indicator powder and a buffer. "Free chlorine" present in the water reacts with the DPD indicator to produce a red to pink coloration. The intensity of the coloration depends upon the concentration of "free chlorine" species present in the sample. This intensity is measured by a colorimeter calibrated to transform the intensity reading into a "free chlorine" value in terms of mg/L Cl₂. Similarly, the "total chlorine" test also involves use of DPD indicator and buffer. In this case, KI is present with the DPD and buffer whereby the halogen species present, including nitrogen-combined halogen, reacts with KI to yield iodine species which turn the DPD indicator to red/pink. The intensity of this coloration depends upon the sum of the "free chlorine" species and all other halogen species present in the sample. Consequently, this coloration is transformed by the colorimeter into a "total chlorine" value expressed as mg/L Cl₂.

5 A halogen water treating agent which could provide a high level of both "free chlorine" and "total chlorine" and where these levels would be close together would be a very desirable water treating agent. Such an agent would be highly effective as a microbiocidal agent and if of an appropriate chemical structure, could be environmentally friendly and highly cost-effective. Pursuant to this invention these criteria are met by the above water-soluble 1,3-dibromo-5,5-dialkylhydantoin (DBDAH).

10 It is to be understood that in the practice of this invention it is not necessary to perform the specified tests every time a body of water is to be dosed with a product in which the biocidally-active ingredient is DBDAH or DBDAH in combination with one or more other biocidally-active ingredients (depending upon the embodiment of this invention being practiced). Instead, the testing should be done when deemed necessary or desirable to either establish the requisite dosage of the product, or to check or confirm that the dosage used complies with the intended level of biocidal protection and thus will make available the economic and environmental benefits resulting from the practice of this invention.

15 When it is desired to conduct the appropriate testing any suitable method of determining "free chlorine" and "total chlorine" can be used, but the full procedure set forth below entitled "DBDAH and BCDMH Test Procedure" is preferably used. Use of such testing will prove to the customer that the use of the biocidal product in the articles of manufacture of this invention actually does release into the water an amount of "free chlorine" that corresponds closely to the "total chlorine" content of the purchased biocidal product.

DBDAH and BCDMH Test Procedure

- 20
1. To determine the amount of species present in the water which respond to the "free chlorine" and "total chlorine" tests, the water sample should be analyzed within a few minutes of being taken, and preferably immediately upon being taken.
 2. Hach Method 8021 for testing the amount of species present in the water sample which respond to the "free chlorine" test involves use of the Hach Model DR 2010
- 25

colorimeter. The stored program number for chlorine determinations is recalled by keying in "80" on the keyboard, followed by setting the absorbance wavelength to 530 nm by rotating the dial on the side of the instrument. Two identical sample cells are filled to the 10 mL mark with the water under investigation. One of the cells is arbitrarily chosen to be the blank. Using the 10 mL cell riser, this is admitted to the sample compartment of the Hach Model DR 2010, and the shield is closed to prevent stray light effects. Then the ZERO key is depressed. After a few seconds, the display registers 0.00 mg/L Cl_2 . To second cell, the contents of a DPD Free Chlorine Powder Pillow are added. This is shaken for 10-20 seconds to mix, as the development of a pink-red color indicates the presence of species in the water which respond positively to the DPD test reagent. Within one minute of adding the DPD "free chlorine" reagent to the 10 mL of water in the sample cell, the blank cell used to zero the instrument is removed from the cell compartment of the Hach Model DR 2010 and replaced with the test sample to which the DPD "free chlorine" test reagent was added. The light shield is then closed as was done for the blank, and the READ key is depressed. The result, in mg/L Cl_2 is shown on the display within a few seconds. This is the "free chlorine" level of the water sample under investigation.

3. Hach Method 8167 for testing the amount of species present in the water sample which respond to the "total chlorine" test involves use of the Hach Model DR 2010 colorimeter. The stored program number for chlorine determinations is recalled by keying in "80" on the keyboard, followed by setting the absorbance wavelength to 530 nm by rotating the dial on the side of the instrument. Two identical sample cells are filled to the 10 mL mark with the water under investigation. One of the cells is arbitrarily chosen to be the blank. To the second cell, the contents of a DPD Total Chlorine Powder Pillow are added. This is shaken for 10-20 seconds to mix, as the development of a pink-red color indicates the presence of species in the water which respond positively to the DPD "total chlorine" test reagent. On the keypad, the SHIFT TIMER keys are depressed to commence a three minute reaction time. After three minutes the instrument beeps to signal the reaction is complete. Using the 10 mL cell

5 riser, the blank sample cell is admitted to the sample compartment of the Hach Model DR 2010, and the shield is closed to prevent stray light effects. Then the ZERO key is depressed. After a few seconds, the display registers 0.00 mg/L Cl_2 . Then, the blank sample cell used to zero the instrument is removed from the cell compartment of the Hach Model DR 2010 and replaced with the test sample to which the DPD "total chlorine" test reagent was added. The light shield is then closed as was done for the blank, and the READ key is depressed. The result, in mg/L Cl_2 is shown on the display within a few seconds. This is the "total chlorine" level of the water sample under investigation.

10 The various new features of this invention and the advantages accruing therefrom will be further apparent from Examples 1-3, which as presented for purposes of illustrating the effectiveness of the invention without limiting the scope of the invention.

EXAMPLE 1

15 Simulated cooling water was prepared using deionized water to which calcium chloride and sodium bicarbonate were added to provide calcium hardness of 400 ppm and a total alkalinity of 300 ppm. A small amount of phosphonobutanetricarboxylic acid (PBTC) (5 ppm) was used to prevent calcium carbonate precipitation. Concentrated sodium hydroxide was added to adjust the pH of the simulated cooling water solutions to pH 9.1.

20 Stock solutions of DBDMH and of BCDMH were prepared by slurring 1 gram of the respective powders in 100 mL of deionized water. After stirring for 20 minutes, the insolubles were filtered to yield clear saturated stock solutions of DBDMH and BCDMH, respectively. Iodometric titration of the stock solutions using the potassium iodide-sodium thiosulfate method indicated the DBDMH solution contained 580 mg/L (as total chlorine), and the BCDMH solution contained 1100 mg/L (as total chlorine).

25 The stock solutions were used to dose two simulated cooling water solutions to 1 mg/L as total chlorine. Thus, 1.7 mL of DBDMH stock solution was introduced to 1000 mL of simulated cooling water to form a first test solution, and 0.91 mL of BCDMH stock solution

was introduced to another 1000 mL of simulated cooling water to produce a second test solution. Both of these test solutions were placed in screw-capped amber bottles to shield from light and prevent evaporation. The bottles were then placed in an oven and heated to 38 °C (100 °F). As soon as the solutions reached the equilibrium temperature of 38 °C, 10 mL aliquots of each test solution were removed and analyzed using Hach Method 8167 for "total chlorine", to confirm that each contained a "total chlorine" level of 1 mg/L. The same solutions were also analyzed using Hach Method 8021 for "free chlorine" to determine how much of the total chlorine species also registered as "free chlorine". These analyses were recorded as results at time 0. The test solutions were then kept in the oven at the equilibrium temperature of 38 °C for a total of 6 hours during which time additional 10 mL aliquots were removed at known time intervals and subjected to the same analysis procedures for "free chlorine" and "total chlorine".

The results of each of the foregoing determinations are summarized in Table 1 and are depicted graphically in Fig. 1. In Table 1 the values given at times 0.5 through 6 hours are percentages of the corresponding values shown in Table 1 for Time 0. These results are depicted graphically in Fig. 1. Table 2 sets forth the percentages of hydrolysis to "free chlorine" experienced by the BCDMH and the DBDMH based on the results shown in Table 1. Fig. 2 depicts the results given in Table 2. It can be seen from Table 2 and Fig. 2 that over a time span of 6 hours the differences in the percentage of hydrolysis as between BCDMH and DBDMH remained substantially constant. The minor variations in such differences appearing in Table 2 and Fig. 2 are deemed insignificant statistically inasmuch as they are within experimental error.

TABLE 1

Time, hr	BCDMH Free Cl ₂	BCDMH Total Cl ₂	DBDMH Free Cl ₂	DBDMH Total Cl ₂
0	23.1	100	98.8	100
0.5	25.6	104	100	104
1	23.1	100	85.1	87.3
1.5	17.9	92.3	87.3	87.3
2	16.6	88.5	81.6	83.9
3	16.6	88.5	70.1	74.7
4	30.7	79.5	65.5	66.6
5	15.4	76.9	60.1	63.2
6	10.2	71	59.8	62

TABLE 2

Time, hr	BCDMH % hydrolysis to Free Cl ₂	DBDMH % hydrolysis to Free Cl ₂
0	23.1	98.8
0.5	24.7	95.6
1	23.1	97.3
1.5	19.4	100
2	18.8	97.2
3	18.8	93.8
4	38.7	93.8
5	20	96.4
6	14.3	96.3

EXAMPLE 2

The effectiveness of DBDMH and of BCDMH in microbiological control in cooling tower water was investigated in comparative tests. The cooling tower consisted of two 500-ton units in a crossflow design. The total system-contained volume was 14,000 gallons, and the tower contained medium efficiency film fill. Water from the tower cooled the coils of two 300-ton air conditioners (chillers). The tower typically operated at a pH of about 9.1 and 4 cycles of concentration. Blowdown was controlled by conductivity. Make-up water consisted of softened city water and which was of good quality. The make-up water was very low in calcium (< 10 mg/L) but high in pH (8.7). The alkalinity was 145 mg/L (as CaCO₃), and the silica level was 28 mg/L. The tower employed a conventional polyphosphate/molybdate/phosphonate program to provide corrosion and deposit control. The conditions and results are summarized in Table 3.

TABLE 3*

	Cooling Tower Water	Make-up Water
<i>Cooling Tower Data</i>		
Temperature (return line)	91 °F	--
Temperature (to process)	83 °F	--
Δ T	8 °F	--
Make-up water	4800 gal/day	--
<i>Water Chemistry</i>		
Conductivity, mS/cm	1.22	0.32
pH, units	9.2	8.7
Alkalinity, mg/L as CaCO ₃	480	145
Total Hardness, mg/L as CaCO ₃	1	3
Silica, mg/L	100	28

*This data represents the average of several analyses conducted during the course of the field trial.

The BCDMH (20 lbs) was introduced to the water using 20-gram, 1-inch tablets charged to a solid halogen feeder (Neptune model BT-40, Neptune Chemical Pump Co., Inc., Lansdale, PA). Before each dose, the cooling tower water was sampled and enumerated for heterotrophic bacteria plate counts. Then the tower was slug dosed three times a week with BCDMH. Slug dosing was accomplished by diverting through the feeder containing the tablets a sidestream of the recirculating water for about 1 to 5 hours until a "free chlorine" dose of about 0.5 mg/L (as "free chlorine") was obtained. The "total chlorine" dose was measured at the same time. After each dose the cooling water was sampled and enumerated for heterotrophic bacteria plate counts. As necessary, the feeder was replenished with more BCDMH tablets. The total dry weight of BCDMH tablets consumed over a 30-day test period (obtained by subtracting the dry weight of the tablets remaining in the feeder at the completion of the test from the total dry weight of the tablets added to the feeder during the test period) was found to be 25 lbs.

It was found that this biocide program (biocide dose 0.5 mg/L "free chlorine") reduced heterotrophic bacterial levels in the bulk water by an average of 1 order of magnitude. For example, before the biocide dose the bacteria levels in the bulk water ranged from 10^5 to 10^4 CFUs/mL. After the biocide dose the bacteria levels in the bulk water were reduced to 10^4 to 10^3 .

After emptying the feeder of BCDMH tablets, 20 lbs of DBDMH granules was charged into the feeder. Thereupon the same procedure as described above for the BCDMH was carried out except for the fact that it was unnecessary to add any additional DBDMH to the feeder during the 30-day test period. In fact, the total weight of DBDMH consumed during the test was only 7 lbs. Also, the targeted 0.5 mg/L "free chlorine" dose in the bulk water was achieved in only 20 to 30 minutes. It was found that the biocidal performance provided by 7 lbs of DBDMH was the same as provided by 25 lbs of BCDMH under the same test conditions.

EXAMPLE 3

Using the same cooling tower as used in Example 2, the effectiveness of 1,3-dibromo-5,5-dimethylhydantoin in microbiological control in cooling tower water was investigated. As noted above, the cooling tower consisted of two 500-ton units in a crossflow design. The total system-contained volume was 14,000 gallons, and the tower contained medium efficiency film fill. Water from the tower cooled the coils of two 300-ton air conditioners (chillers). The tower typically operated at a pH of about 9.1 and 4 cycles of concentration. Blowdown was controlled by conductivity. Make-up water consisted of softened city water and which was of good quality. The make-up water was very low in calcium (< 10 mg/L) but high in pH (8.7). The alkalinity was 145 mg/L (as CaCO_3), and the silica level was 28 mg/L. The tower employed a conventional polyphosphate/molybdate/phosphonate program to provide corrosion and deposit control.

The 1,3-dibromo-5,5-dimethylhydantoin was introduced to the water using granules charged to a solid halogen feeder (Neptune model BT-40, Neptune Chemical Pump Co., Inc., Lansdale, PA). The field trial lasted 51 days. The tower was slug dosed three times a week with 1,3-dibromo-5,5-dimethylhydantoin. Slug dosing was accomplished by diverting a sidestream of the recirculating water through the feeder containing the granules for about 1 to 5 hours until a total halogen residual of about 0.75 mg/L (as Cl_2) was obtained. This biocide program reduced bacterial levels in the bulk water by an average of 2 orders of magnitude, with bacteria levels in the bulk water after the biocide dose ranging from 10^1 to 10^3 CFUs/mL.

The results from the average of several analyses conducted during the course of this field trial using DBDMH were as follows: In the microbiological tests, the levels of aerobic bacteria were in the range of 6×10^0 to 3×10^3 CFUs/mL in the cooling tower water and 10^0 in the make-up water. As regards water chemistry, the free halogen residual (as Cl_2) was 0.79 mg/L (the range being 1.9 - 0.00 mg/L) in the cooling tower water and 0.05 mg/L in the make-up water; and the total halogen residual (as Cl_2) was 0.82 mg/L (the range being 1.9 - 0.03 mg/L) in the cooling tower water and 0.8 mg/L in the make-up water.

5 The packaged biocide of this invention, whether DBDAH is the only biocidally-active ingredient or is in combination with one or more other compatible biocidally-active ingredients, can be in the form of a powder, granules, nuggets, caplets, pellets, tablets, briquettes, or pucks. A preferred process for producing highly suitable powder or particulate DBDMH and novel DBDMH products are described respectively in commonly-owned
10 copending Application Nos. 09/484,844 and 09/484,687, both filed January 18, 2000. Methods for the formation of compacted forms of DBDMH such as caplets, tablets, briquettes and pucks are described in commonly-owned copending Application No. 09/487,816, filed January 18, 2000. Methods for producing DBDMH in granular form are described in commonly-owned copending Application No. 09/483,896, filed January 18, 2000. The disclosures of each of the foregoing applications are incorporated herein by reference as if fully set forth herein.

15 When the packaged biocidal product of this invention contains as the sole active ingredient 1,3-dibromo-5,5-dimethylhydantoin in a compacted form, such compacted form can be produced without use of a binder provided that the average particle size of the 1,3-dibromo-5,5-dimethylhydantoin (DBDMH) is at least 175 microns. Alternatively and more preferably, the compacted forms of DBDMH, and in fact of any and all DBDAH, are produced with use of a binder. As noted above, preferred binders are described in U.S. Pat. No. 5,565,576, issued October 15, 1996, the disclosure of which patent is incorporated herein
20 *in toto* as if fully set forth herein. Preferably such fatty amide binder is used with 1,3-dibromo-5,5-dimethylhydantoin having an average particle size of at least 175 microns. As also noted above, particularly preferred types of binder for use in producing the compacted forms of DBDMH or DBDAH is a micronized synthetic polyolefin-based hydrocarbon wax and/or a micronized synthetic polyfluorocarbon wax effective to form the compacted product,
25 provided the wax is suitably compatible with the DBDMH or DBDAH.

The amount of the packaged biocides of this invention used is a biocidally effective amount, *e.g.*, an amount which is at least sufficient to achieve substantial microbiological

control, if not complete microbiological control, in the water being treated and/or substantial biofilm eradication, if not complete biofilm eradication, from the surfaces in contact with the water system being treated. Such dosage level is preferably indicated on the label of the package. Typically, the dosages will fall within the range of about 0.1 to about 4.5 milligrams of "free chlorine" per liter of water (which corresponds to about 0.2 to about 10 milligrams of bromine, as Br₂, per liter of water). Preferably, such dosages are in the range of about 0.1 to about 2 milligrams of "free chlorine" per liter of water (which corresponds to about 0.2 to about 5 milligrams of bromine, as Br₂, per liter of water). However, departures from these ranges are permissible and are within the scope of this invention, provided that the departures result in sufficient microbiological control in accordance with the needs of the occasion, including applicable governmental regulations.

The efficacy of the packaged biocidal compositions of this invention in control of microbial infestations, was demonstrated in a series of tests was conducted at an independent microbiology and virology laboratory. *Escherichia coli* and *Enterococcus faecium* were the pathogens used in this study. One such series of tests utilized the AOAC Official Method, involved determinations of microbiological control against the *E. coli* bacteria. The other set of tests involved determinations of microbiological control against the *E. faecium*. In each case, comparative tests were carried out in the same manner utilizing N,N'-bromochloro-5,5-dimethylhydantoin. Briefly, the test involves exposing a culture of the microorganism to various concentrations of bromine solution prepared from an aqueous stock solution of the compound under test. At various time intervals the bromine in the test suspensions is chemically neutralized, and the amount of viable bacteria remaining is enumerated by plating onto nutrient agar and incubating for 2 days at 37°C. Results are expressed at the log₁₀ colony forming units (CFU). The concentration of the compound required to achieve complete kill (*i.e.*, no viable bacteria remain) within 30 seconds is determined in the test and reported to the U.S. Environmental Protection Agency to support the product registration as a disinfectant for swimming pools. Such testing is one of the requirements needed for product

registration with the EPA, which in turn enables the product to be purveyed with labeling showing the efficacious dosage level of the product.

Table 4 summarizes the data obtained in the tests using respectively, 1,3-dibromo-5,5-dimethylhydantoin (DBDMH) and N,N'-bromochloro-5,5-dimethylhydantoin (BCDMH) and in which the microorganism in each case was *E. coli*. It can be seen that 1,3-dibromo-5,5-dimethylhydantoin passes the test at one milligram of bromine, as Br₂, per liter of water, as evidenced by the complete kill within 30 seconds, whereas 1,3-bromochloro-5,5-dimethylhydantoin requires two milligrams of bromine, as Br₂, per liter of water to achieve complete kill within 30 seconds.

TABLE 4 - EFFECTIVENESS AGAINST *E. COLI*

Concentration mg/L as Br ₂	Contact Time	Log ₁₀ CFU Recovered Using DBDMH	Log ₁₀ CFU Recovered Using BCDMH
0.5 mg/L	30 sec	>4.48	>4.48
	1 min	1.70	4.46
	2 min	0	1.65
	3 min	0	0
	4 min	0	0
	5 min	0	0
	10 min	0	0
1.0 mg/L	30 sec	0	>4.48
	1 min	0	0.7
	2 min	0	0
	3 min	0	0
	4 min	0	0
	5 min	0	0
	10 min	0	0

2.0 mg/L	30 sec	0	0
	1 min	0	0
	2 min	0	0
	3 min	0	0
	4 min	0	0
	5 min	0	0
	10 min	0	0

Table 5 summarizes the data obtained in the tests using respectively 1,3-dibromo-5,5-dimethylhydantoin (DBDMH) and N,N'-bromochloro-5,5-dimethylhydantoin (BCDMH) and in which the microorganism in each case was *E. faecium*. Table 5 shows that 1,3-dibromo-5,5-dimethylhydantoin passes the test at one milligram of bromine, as Br₂, per liter of water, as evidenced by the complete kill within 30 seconds, whereas N,N'-bromochloro-5,5-dimethylhydantoin requires two milligrams of bromine, as Br₂, per liter of water to achieve complete kill within 30 seconds.

TABLE 5 - EFFECTIVENESS AGAINST *E. FAECIUM*

Concentration mg/L as Br ₂	Contact Time	Log ₁₀ CFU Recovered Using DBDMH	Log ₁₀ CFU Recovered Using BCDMH
0.5 mg/L	30 sec	4.32	>4.48
	1 min	2.36	3.53
	2 min	0	2.63
	3 min	0	0
	4 min	0	0
	5 min	0	0
	10 min	0	0

1.0 mg/L	30 sec	0	>4.48
	1 min	0	2.38
	2 min	0	0
	3 min	0	0
	4 min	0	0
	5 min	0	0
	10 min	0	0
2.0 mg/L	30 sec	0	0
	1 min	0	0
	2 min	0	0
	3 min	0	0
	4 min	0	0
	5 min	0	0
	10 min	0	0

As noted above, the most effective presently-known process for producing 1,3-dibromo-5,5-dimethylhydantoin for use in the practice of this invention is described in commonly-owned copending Application No. 09/484,844, filed January 18, 2000. That process comprises, for example, concurrently feeding (i) an aqueous solution or slurry formed from an inorganic base and 5,5-dimethylhydantoin, and (ii) a brominating agent in proportions such that each nitrogen atom is substituted by a bromine atom, thereby continuously forming product which precipitates in an aqueous reaction mixture. The pH of the mixture is continuously maintained in the range of about 5.5 to about 8.5. Examples 4-14 below illustrate that process. In Examples 4-14, pH was monitored by use of a pH meter. In Examples 4-13, bromine was fed using a Cole-Parmer Masterflex computerized drive and Easy-Load[®] pump head. When conducting the continuous operations of Examples 12 and 13, the resulting reaction slurry was collected manually and intermittently from the bottom of the

reactor. Each fraction was collected in a 500 mL flask. These Examples do not constitute part of this invention. Instead they are presented to show best ways of making DBDMH.

EXAMPLE 4

235 Grams of NaOH (5.85 mol) are dissolved in 1800g of water, and 375g of 5,5-dimethylhydantoin (2.93 mol) is added to the NaOH solution. There are 935g of Br₂ (5.85 mol) in the bromine reservoir. A 1-liter jacketed flask into which the Br₂ and the 5,5-dimethylhydantoin/NaOH solution are fed is maintained at 25 °C with a cooling bath. The 5,5-dimethylhydantoin/NaOH solution is co-fed to the reaction flask simultaneously with, but separately from, Br₂. The feed of the 5,5-dimethylhydantoin/NaOH solution was initiated shortly before (*e.g.*, 3-4 min.) the initiation of the Br₂ feed. The feed rate of the 5,5-dimethylhydantoin/NaOH solution is 10 mL/minute, and the feed rate of the Br₂ is 1.60-1.70 mL/minute. The reaction mixture is stirred with a mechanical stirrer at a rate of 350-400 rpm. During the reaction, the pH ranged from 7.4 to 7.9. The slurry that forms as the reaction progresses is collected at a rate such that the level of the solution in the reaction flask remains constant. 500 mL fractions of product are collected through the bottom of the reaction flask, in an average time of 30 minutes per fraction. When the 5,5-dimethylhydantoin/NaOH solution feed is finished, 86g of Br₂ (0.54 mol) remains in the bromine reservoir.

Each product fraction is filtered and washed with three 500 mL portions of water, and the solid is then dried under a stream of nitrogen. The isolated yield of 1,3-dibromo-5,5-dimethylhydantoin is 673g, a yield of 80% based on 5,5-dimethylhydantoin, or a yield of 89% based on Br₂. The active bromine content is at least 99%, as determined by iodometric titration.

EXAMPLE 5

44 Grams of NaOH (1.1 mol) are dissolved in 338g of water, and 70.4g of 5,5-dimethylhydantoin (0.55 mol) is added to the NaOH solution. There are 175.1g of Br₂ (1.1 mol) in the bromine reservoir. The reaction flask into which the Br₂ and the 5,5-dimethylhydantoin/NaOH solution are fed is maintained at 35 °C with a heating bath. The

reaction flask is charged with ~200 mL heel (238g) of a 1,3-dibromo-5,5-dimethylhydantoin filtrate (mother liquor). The 5,5-dimethylhydantoin/NaOH solution is co-fed to the reaction flask simultaneously with, but separately from, Br₂. The reaction mixture is stirred with a mechanical stirrer at a rate of 400 rpm. During the reaction, the pH ranged from 6.9 to 8.0. The reaction temperature stabilized at 37°C during the 0.5 hour addition time. When the addition of reagents is finished, the orange slurry is filtered at 35°C and washed with 650 mL of water. The resultant white solid is dried overnight under a stream of nitrogen. The isolated yield of 1,3-dibromo-5,5-dimethylhydantoin is 147.6g, a yield of 94%, and the active bromine content of the 1,3-dibromo-5,5-dimethylhydantoin is 55.1 wt% (98.6% of the theoretical value), as determined by iodometric titration.

EXAMPLE 6

44 Grams of NaOH (1.1 mol) are dissolved in 338g of water, and 70.4g of 5,5-dimethylhydantoin (0.55 mol) is added to the NaOH solution. There are 172.0g of Br₂ (1.07 mol) in the bromine reservoir. The reaction flask into which the Br₂ and the 5,5-dimethylhydantoin/NaOH solution are fed is maintained at 67°C with a heating bath. The reaction flask is charged with ~200 mL heel (238g) of a 1,3-dibromo-5,5-dimethylhydantoin filtrate (mother liquor). The 5,5-dimethylhydantoin/NaOH solution is co-fed to the reaction flask simultaneously with, but separately from, Br₂. The bromine is diluted with nitrogen and fed below the surface of the solution in the reaction flask. The reaction mixture is stirred with a mechanical stirrer at a rate of 400 rpm; the pH ranged from 6.7 to 7.1 during the reaction. During the 0.5 hour addition time, the reaction temperature stabilized at 67°C. When the addition of reagents is finished, the orange slurry is discharged from the reaction flask into a beaker and allowed to cool slowly. The slurry is filtered at ~45°C and washed with two 500 mL portions of water. The resultant white solid is dried overnight under a stream of nitrogen. The isolated yield of 1,3-dibromo-5,5-dimethylhydantoin is 130.5g, a yield of ~83% based on 5,5-dimethylhydantoin, or a yield of ~85% based on Br₂. The active bromine content of the 1,3-dibromo-5,5-dimethylhydantoin is 55.9 wt% (100% of the theoretical value), as

determined by iodometric titration. Particle size data on the 1,3-dibromo-5,5-dimethylhydantoin product formed in this operation based on a representative dried sample of the product are summarized in Table 6.

TABLE 6

Particle Size Category	Particle Size of Product
Average	237.5 μ
10% is greater than	371.6 μ
25% is greater than	309.8 μ
50% is greater than	239.1 μ
75% is greater than	165.6 μ
90% is greater than	99.81 μ
Range	0.040-541.9 μ

EXAMPLE 7

354 Grams of NaOH (8.85 mol) are dissolved in 2700g of water. 562g of 5,5-dimethylhydantoin (4.386 mol) is added to the NaOH solution. The reaction flask is charged with 500 mL heel of a 1,3-dibromo-5,5-dimethylhydantoin filtrate (mother liquor). The 5,5-dimethylhydantoin/NaOH solution is co-fed to the jacketed reaction flask, no heating or cooling is applied simultaneously with, but separately from, Br₂. The feed rate of the 5,5-dimethylhydantoin/NaOH solution is 10 mL/minute, and the feed rate of the Br₂ is initially 1.70 mL/minute, but is adjusted later to 1.68 mL/minute to maintain the pH of the reaction mixture at ~7.0. The reaction mixture is stirred with a mechanical stirrer at a rate of 400 rpm reaction temperature is stabilized at about 42°C. The slurry that forms as the reaction progresses is collected at a rate such that the level of the solution in the reaction flask remains constant. Eight 500 mL fractions of product were collected through the bottom of the reaction flask, in an average time of 30 minutes per fraction. A total of 1374.5g of Br₂ (8.59 mol) are added during the reaction.

Each product fraction is filtered and washed with a 500 mL portion of water; the solids are then dried overnight at 50 °C in a vacuum oven. The total isolated yield of 1,3-dibromo-5,5-dimethylhydantoin is 1152g, a yield of 92% based on 5,5-dimethylhydantoin, or a yield of 94% based on Br₂. The active bromine content of the 1,3-dibromo-5,5-dimethylhydantoin ranges from 55.4 wt% to 55.7 wt% (99.1% to 99.7% of the theoretical value), as determined by iodometric titration. The average particle size of the 1,3-dibromo-5,5-dimethylhydantoin is greater than 150μ.

EXAMPLE 8

89 Grams of NaOH (2.2 mol) are dissolved in 676g of water, and 141g of 5,5-dimethylhydantoin (1.1 mol) is added to the NaOH solution. There are 350g of Br₂ (2.2 mol) in the bromine reservoir. The reaction flask into which the Br₂ and the 5,5-dimethylhydantoin/NaOH solution are fed is maintained at 67 °C with a heating bath. The reaction flask is charged with ~400 mL heel (483g) of a 1,3-dibromo-5,5-dimethylhydantoin filtrate (mother liquor). The 5,5-dimethylhydantoin/NaOH solution is co-fed to the reaction flask simultaneously with, but separately from, Br₂. The reaction mixture is stirred with a mechanical stirrer at a rate of 400 rpm. During the reaction, the pH ranged from 6.8 to 7.1. The reaction temperature stabilized at 67 °C during the 66 minute addition time. When the addition of reagents is finished, the orange slurry is filtered at 43 °C and washed with 1000 mL (2x500 mL) of water. The resultant white solid is dried overnight under a stream of nitrogen. 307.3 Grams of Br₂ (1.92 mol) had been fed to the reaction flask. The isolated yield of 1,3-dibromo-5,5-dimethylhydantoin is 212.5g, a yield of 77% based on Br₂, and 68% based on 5,5-dimethylhydantoin; the active bromine content of the 1,3-dibromo-5,5-dimethylhydantoin is 55.9 wt% (100% of the theoretical value), as determined by iodometric titration.

EXAMPLE 9

88 Grams of NaOH (2.2 mol) are dissolved in 338g of water, and 140.8g of 5,5-dimethylhydantoin (1.1 mol) is added to the NaOH solution. There are 352g of Br₂ (2.2 mol) in the bromine reservoir. The reaction flask into which the Br₂ and the 5,5-dimethylhydantoin/NaOH solution are fed is maintained at 69°C with a heating bath. The reaction flask is charged with ~200 mL heel (240g) of a 1,3-dibromo-5,5-dimethylhydantoin filtrate (mother liquor). The 5,5-dimethylhydantoin/NaOH solution is co-fed to the reaction flask simultaneously with, but separately from, Br₂. The reaction mixture is stirred with a mechanical stirrer at a rate of 400 rpm. During the reaction, the pH ranged from 6.8 to 7.0. The reaction temperature stabilized at 68-69°C during the 39 minute addition time. When the addition of reagents is finished, the orange slurry is filtered at 40°C and washed with 500 mL of water. The resultant white solid is dried overnight under a stream of nitrogen. 285.5 Grams of Br₂ (1.78 mol) had been fed to the reaction flask. The isolated yield of 1,3-dibromo-5,5-dimethylhydantoin is 186.8g, a yield of 73% based on Br₂, and 60% based on 5,5-dimethylhydantoin; the active bromine content of the 1,3-dibromo-5,5-dimethylhydantoin is 53.4 wt% (96% of the theoretical value), as determined by iodometric titration.

Table 7 summarizes the particle size data for the products of Examples 8 and 9.

TABLE 7

Particle Size Category	Particle Size of Product - Example 8	Particle Size of Product - Example 9
Average	210.4μ	293.6μ
10% is greater than	381.7μ	451.2μ
25% is greater than	298.3μ	349.6μ
50% is greater than	196.8μ	256.3μ
75% is greater than	115.3μ	174.9μ
90% is greater than	56.86μ	110.6μ
Range	0.040-594.9μ	0.040- >2000μ

EXAMPLE 10

44.2 Grams of NaOH (1.1 mol) are dissolved in 338g of water, and 70.4g of 5,5-dimethylhydantoin (0.55 mol) is added to the NaOH solution. There are 173g of Br₂ (1.08 mol) in the bromine reservoir. The reaction flask into which the Br₂ and the 5,5-dimethylhydantoin/NaOH solution are fed is maintained at 57°C with a heating bath. The reaction flask is charged with ~200 mL heel (244g) of a 1,3-dibromo-5,5-dimethylhydantoin filtrate (mother liquor). The 5,5-dimethylhydantoin/NaOH solution is co-fed to the reaction flask simultaneously with, but separately from, Br₂. The reaction mixture is stirred with a mechanical stirrer at a rate of 400 rpm. During the reaction, the pH ranged from 6.8 to 7.2. Maintenance of the desired pH was accomplished by adjusting the bromine feed rate. The reaction temperature stabilized at 57°C during the 33 minute addition time. When the addition of reagents is finished, the orange slurry is filtered at 38°C and washed with 500 mL of water. The resultant white solid is dried overnight under a stream of nitrogen. The isolated yield of 1,3-dibromo-5,5-dimethylhydantoin is 139.8g, a yield of 91% based on Br₂, and 89% based on 5,5-dimethylhydantoin; the active bromine content of the 1,3-dibromo-5,5-dimethylhydantoin is 55.7 wt% (99.7% of the theoretical value), as determined by iodometric titration.

EXAMPLE 11

44.2 Grams of NaOH (1.1 mol) are dissolved in 338g of water, and 70.3g of 5,5-dimethylhydantoin (0.55 mol) is added to the NaOH solution. There are 172.5g of Br₂ (1.08 mol) in the bromine reservoir. The reaction flask into which the Br₂ and the 5,5-dimethylhydantoin/NaOH solution are fed is maintained at 48°C with a heating bath. The reaction flask is charged with ~200 mL heel of a 1,3-dibromo-5,5-dimethylhydantoin filtrate (mother liquor). The 5,5-dimethylhydantoin/NaOH solution is co-fed to the reaction flask simultaneously with, but separately from, Br₂. The reaction mixture is stirred with a mechanical stirrer at a rate of 400 rpm. During the reaction, the pH ranged from 6.8 to 7.2. Maintenance of the desired pH was accomplished by adjusting the bromine feed rate. The

species formed during the water treatment operation. In other words, the chlorine atom in the initial N,N'-bromochloro-5,5-dialkylhydantoin is said to be a precursor for additional "free chlorine" for sanitation purposes.

5 In use, BCDMH hydrolyzes into HOBr and HOCl both of which register as "free chlorine" species in commonly-used standard test procedures. These methods for determining "free chlorine" levels in treated water, involve use of a reagent known as DPD (*i.e.*, N,N'-diethyldiphenylenediamine) and a buffer, and the results of such analyses are commonly used, if not universally used, as the basis for determining the quantity of a halogen-containing microbiocidal agent to be used for water treatment. Heretofore, consumers of BCDMH have only been concerned with the level of "free chlorine" provided by a given quantity of that biocidal material. What has not been realized by such consumers is the amount of "total chlorine" being utilized in order to achieve the requisite "free chlorine" level. As a consequence, the consumer has not had available a yardstick by which to determine the true economic efficiency of using BCDMH as a biocidal agent in the treatment of water. To achieve optimum economic efficiency, the consumer should have available for use a biocidal agent in which the amount of "free chlorine" released into the water corresponds closely to the "total chlorine" content of the biocidal agent.

20 In the event a biocidal agent provides a relatively small amount of "free chlorine" in relation to its "total chlorine" content, it has been deemed necessary to utilize a relatively large amount of such agent in order to achieve microbiological control. This in turn means high levels of halogenated materials are released into the environment. If on the other hand, a biocidal agent could provide to the water an amount of "free chlorine" that closely corresponds to the "total chlorine" content of the biocidal agent, effective microbiological control could be realized by use of much smaller dosages and with consequent minimal
25 adverse impact upon the environment.

reaction temperature stabilized at 48°C during the 34 minute addition time. When the addition of reagents is finished, the orange slurry is filtered at 38°C and washed with 500 mL of water. The resultant white solid is dried overnight under a stream of nitrogen. The isolated yield of 1,3-dibromo-5,5-dimethylhydantoin is 144.8g, a yield of 94% based on Br₂, and 92% based on 5,5-dimethylhydantoin; the active bromine content of the 1,3-dibromo-5,5-dimethylhydantoin is 55.0 wt% (98.4% of the theoretical value), as determined by iodometric titration.

The particle size data for the products of Examples 10 and 11 are summarized in Table 8.

TABLE 8

Particle Size Category	Particle Size of Product - Example 10	Particle Size of Product - Example 11
Average	231.2μ	178.4μ
10% is greater than	338.3μ	281.1μ
25% is greater than	285.0μ	230.9μ
50% is greater than	228.8μ	175.7μ
75% is greater than	177.8μ	125.0μ
90% is greater than	133.0μ	79.14μ
Range	0.040-493.6μ	0.040-409.6μ

EXAMPLE 12

The process of this Example was conducted in a continuous fashion. A feed solution of 5,5-dimethylhydantoin/NaOH was formed by adding 5,5-dimethylhydantoin to a 9 wt% NaOH solution, such that the 5,5-dimethylhydantoin concentration was about 1.1 M. The 5,5-dimethylhydantoin/NaOH solution was co-fed to the reaction flask simultaneously with, but separately from, Br₂. The flask was suspended in a heating bath. The reaction mixture was stirred with a mechanical stirrer at a rate of 500 rpm. The reaction mixture was maintained

at a pH of about 7.0 ± 0.2 , and the reaction temperature was maintained at 55°C . Ten fractions of product were collected in an average time of 30 minutes per fraction. The isolated yield of the 1,3-dibromo-5,5-dimethylhydantoin was 90% based on 5,5-dimethylhydantoin, and 92% based on added Br_2 . The purity of the 1,3-dibromo-5,5-dimethylhydantoin, a white crystalline product, was 99.8%, based on the theoretical bromine content. Fractions 5-10 represent the particle size of the product as formed during steady-state operating conditions. Table 9 summarizes average particle size data and particle size distribution data relating to fractions 5-10 based on samples of each such fraction taken during the steady-state operation of the continuous process. The determinations showed that a bimodal distribution of the product had been produced. The overall average particle size of the product was 512.3 microns.

TABLE 9

Particle Size	Fraction 5	Fraction 6	Fraction 7	Fraction 8	Fractions 9+10
Average	371.7 μ	445.6 μ	535.5 μ	560.3 μ	545.9 μ
10% is greater than	530.7 μ	626.0 μ	724.7 μ	805.0 μ	952.1 μ
25% is greater than	462.2 μ	550.9 μ	643.3 μ	729.3 μ	833.4 μ
50% is greater than	386.0 μ	474.5 μ	559.7 μ	641.8 μ	676.7 μ
75% is greater than	256.8 μ	369.6 μ	447.8 μ	436.1 μ	149.6 μ
90% is greater than	94.76 μ	134.4 μ	150.3 μ	94.5 μ	76.02 μ
Range	0.791-786.9 μ ; 1255-1512 μ	4.241-786.9 μ ; 1143-1255 μ	3.519-863.9 μ ; 1143-1512 μ	3.519-8.639 μ ; 1143-1512 μ	0.721-409.6 μ ; 493.6-1255 μ

EXAMPLE 13

Another continuous operation was conducted in a manner similar to that of Example 12. The feed solution was formed by dissolving 355g (8.87 mols) in 3550g of water. To this was added 560g (4.37 mols) of 5,5-dimethylhydantoin. The concurrent feeds were adjusted to maintain the pH of the aqueous reaction mixture at 7.0 ± 0.2 . The temperature was maintained at 55°C . The total amount of bromine (Br_2) fed was 1359.4g (8.50 mols). As in Example 12, ten fractions of the reaction mixture were collected. However, in this operation, the addition rates were adjusted such that the average residence time was approximately 1 hour per fraction. The total isolated yield of 1,3-dibromo-5,5-dimethylhydantoin was 88% based on 5,5-dimethylhydantoin used and 90% based on the added bromine. The 1,3-dibromo-5,5-dimethylhydantoin product was obtained as a white crystalline solid. Table 10 summarizes the average particle size data and product distribution data relating to the product formed in this reaction. Fractions 5-10 represent the particle size of the product as formed during steady-state operating conditions. As in Example 12, the product formed was bimodal. In Table 10 "n.d." indicates that the particle size determination for the larger particle sized fraction was not determined; the instrument used could not measure particles having a particle size greater than 2000 microns. The overall average particle size of the product was at least 455.5 microns.

TABLE 10

Particle Size	Fraction 5	Fraction 6	Fraction 7	Fraction 8	Fractions 9+10
Average	421.2 μ	478.6 μ	494.0 μ	536.6 μ	631.9 μ
10% is greater than	606.5 μ	699.1 μ	781.7 μ	1063 μ	1438 μ
25% is greater than	532.1 μ	623.4 μ	681.5 μ	813.9 μ	995.7 μ
50% is greater than	452.3 μ	535.0 μ	548.5 μ	546.7 μ	522.8
75% is greater than	340.0 μ	372.2 μ	176.6 μ	150.3 μ	160.7 μ

90% is greater than	140.8 μ	112.8 μ	68.94 μ	72.93	81.68 μ
Range	2.423-786.9 μ ; n.d.	2.423-863.9 μ ; n.d.	1.520-863.9 μ ; 1255-1512 μ	0.04-2000 μ ; n.d.	0.04->2000 μ ; n.d.

EXAMPLE 14

Another continuous operation was performed using a glass reactor into which were concurrently fed, on a continuous basis, an aqueous solution formed from 5,5-dimethylhydantoin and NaOH, and a separate feed of bromine. The aqueous solution was made by adding 5,5-dimethylhydantoin to an aqueous 9 wt% NaOH solution. This solution contained about 22.4 wt% of 5,5-dimethylhydantoin and 7 wt% NaOH. A one liter, jacketed reactor having an interior diameter of 82 millimeters equipped with an anchor agitator, with an outer diameter of 72 millimeters, was used, and a silicone fluid (Rhodersil 4720V20 fluid; Rhone-Poulenc) was circulated through the jacketing. The temperature of the reaction was controlled at 38°C. Both feeds were controlled by pumps; the average feed rate of the 5,5-dimethylhydantoin/NaOH solution was 15.84 grams/minute *via* a Prominent Gamma G/4A positive displacement pump, and the average feed rate of the bromine was 4.67 grams/minute *via* a Masterflex Easy-Load peristaltic pump. The reaction mixture was stirred at 400 rpm. The pH of the reaction was monitored by measuring the pH of the effluent using a pH meter, and the pH ranged from 6.06 to 6.36 during the reaction. Product removal from the reactor was also controlled by a pump. Residence time was, on average, 30 minutes per fraction; each fraction was about 500 mL. A yield of 90.5% of 1,3-dibromo-5,5-dimethylhydantoin was obtained, based on the amount of 5,5-dimethylhydantoin fed to the reactor. The active bromine content of the 1,3-dibromo-5,5-dimethylhydantoin was >55.3%, as determined by standard iodometric titration. Thus, the purity of this product was greater than 99.0%.

Table 11 summarizes particle size data on the 1,3-dibromo-5,5-dimethylhydantoin product formed in the continuous operation of Example 14. These data are averaged data

based on two samples taken at different times during the continuous operation once steady state conditions, or essentially steady state conditions, had been achieved.

TABLE 11

Particle Size Category	Particle Size of Product
Average	188.9 μ
10% is greater than	295.2 μ
25% is greater than	255.6 μ
50% is greater than	203.1 μ
75% is greater than	122.5 μ
90% is greater than	55.9 μ
Range	0.872 - 356.5 μ

Examples 15 and 16 illustrate methods of producing tablets from large average particle size 1,3-dibromo-5,5-dimethylhydantoin without use of binders, and the exceptional crush strength of such binder-free tablets. Example 17 illustrates the excellent flowability characteristics and low-dusting properties possessed by the large average particle size 1,3-dibromo-5,5-dimethylhydantoin.

EXAMPLE 15

Five gram samples of 1,3-dibromo-5,5-dimethylhydantoin produced by the process referred to above were compacted without binder in a Sintech[®] press (MTS Systems Corporation, Edenprairie, Minnesota) equipped with a punch and die fabricated from Hastelloy[®] C alloy. Prior to filling the die, the interior surfaces of the die were lightly dusted with a micronized polypropylene wax (MICROPRO 400 wax; Micro Powders, Incorporated, Tarrytown, NY) to serve as a lubricant. The pressure applied was 5000 psi with no dwell time, *i.e.*, the pressure was automatically terminated immediately upon reaching 5000 psi. The resultant tablets after removal from the die were aged for 6 days at room temperature. Thereupon the tablets were subjected to crush strength testing utilizing a Sintech[®] 1/S

compression apparatus (MTS Systems Corporation, Edenprairie, Minnesota) equipped with Testworks software, which software is installed in the 1/S compression apparatus as supplied by MTS Systems Corporation. The apparatus includes a horizontal circular-shaped load cell interfaced with a computer, a digital micrometer also interfaced with the computer, and a vertical screw-driven piston that is disposed above the load cell and adapted to apply a downward force perpendicular to the load cell. The procedure for measuring crush strength involves measuring the thickness of the tablet with the micrometer to provide a digitized input to the computer. Next the tablet is placed on its edge on the load cell with the piston in contact with the upper edge of the tablet. Then the apparatus is activated whereby the piston commences applying a progressively increasing downward diametral force to the tablet. At the same time, the load cell continuously measures the downward force being applied to the tablet, and the input of such measurements is transmitted to the computer. When the force being applied reaches the point where the amount of force suddenly decreases to 10% of the immediately preceding force, the tablet has reached the breaking point, and the application of the force is immediately terminated by the software program. From the inputs to the computer, two values are provided, namely the pounds of force at the breaking point of the tablet, and the pounds of force per inch thickness of the tablet at the breaking point. Thus the greater the force applied, the greater the strength. Two groups of such tests were conducted. One set (Set A) involved forming and evaluating 5 tablets from a batch of 1,3-dibromo-5,5-dimethylhydantoin produced in a continuous process described in Example 13. The other set (Set B) of tests involved 3 tablets produced from another batch of 1,3-dibromo-5,5-dimethylhydantoin produced in a batch process of the type described in Example 9. Table 12 summarizes the results of these tests.

TABLE 12

Test Set	Tablet Thickness	Crush Strength	Crush Strength
A	0.365 in.	20.9 lb.	57.3 lb./in.
A	0.367 in.	25.5 lb.	69.5 lb./in.
A	0.366 in.	19.2 lb.	52.5 lb./in.

A	0.367 in.	22.8 lb.	62.1 lb./in.
A	0.364 in.	23.7 lb.	65.0 lb./in.
Avg. of A	---	22.4 lb.	61.3 lb./in.
B	0.353 in.	10.7 lb.	30.4 lb./in.
B	0.352 in.	12.8 lb.	36.4 lb./in.
B	0.354 in.	9.8 lb.	27.8 lb./in.
Avg. of B	---	11.1 lb.	31.5 lb./in.

Tablets of conventional, small particle sized 1,3-dibromo-5,5-dimethylhydantoin devoid of binder cannot be tableted in the manner described above.

EXAMPLE 16

The crush strength of tablets formed from 1,3-dibromo-5,5-dimethylhydantoin formulated with a binder was illustrated in a group of tests conducted as described in Example 15. The procedure for producing the tablets was as follows: 1,3-dibromo-5,5-dimethylhydantoin produced as in Example 14 was hand-mixed with 3% by weight of micronized polyethylene wax from Micro Powders Incorporated, Tarrytown, NY for approximately 30 minutes. The resultant formulation was then converted into tablets as described in Example 15. The results of the crush strength tests, conducted as described in Example 15, are summarized in Table 13.

TABLE 13

Tablet Thickness	Crush Strength	Crush Strength
0.372 in.	39.8 lb.	107.2 lb./in.
0.375 in.	44.9 lb.	119.9 lb./in.
0.375 in.	37.5 lb.	100.0 lb./in.
0.375 in.	36.1 lb.	96.5 lb./in.
0.377 in.	37.6 lb.	99.7 lb./in.
Averaged Results	39.2 lb.	104.6 lb./in.

EXAMPLE 17

Comparative flowability tests were carried out using a sample of 1,3-dibromo-5,5-dimethylhydantoin and samples of commercially-available 1,3-dihalo-5,5-dimethylhydantoin products. These tests involved filling an 8-ounce glass jar to about one-third of its capacity with the sample to be tested. After closing the jar, it was slowly rotated while on its side in a single direction while observing the characteristics of the contents. Table 14 summarizes the observations made in these flowability tests. In Table 14 the following abbreviations are used:

DBDMH is 1,3-dibromo-5,5-dimethylhydantoin

DCDMH is 1,3-dichloro-5,5-dimethylhydantoin

BCDMH is N,N'-bromochloro-5,5-dimethylhydantoin

TABLE 14

N,N'-dihalo-5,5-dimethylhydantoin	Average Particle Size	Source	Product Characteristics
DCDMH	108.1 microns	Aldrich Chemical Co.	Bridging occurred; high dusting, non-free-flowing powder
BCDMH	323.8 microns	Aldrich Chemical Co.	Bridging occurred; high dusting, non-free-flowing powder
DBDMH	162.1 microns	Aldrich Chemical Co.	Bridging occurred; high dusting, non-free-flowing powder
DBDMH	64.5 microns	Albemarle Corporation	Bridging occurred; high dusting, non-free-flowing powder
DBDMH	45.2 microns	Great Lakes Chemical Corporation	Bridging occurred; high dusting, non-free-flowing powder
DBDMH	293.6 microns	The new process of Application No. 09/484,844	No bridging occurred; low dusting, free-flowing powder

Examples 18-26 illustrate the preparation and properties of compacted products formed from 1,3-dibromo-5,5-dimethylhydantoin utilizing novel binders as described in commonly-owned copending Application No. 09/487,816, filed January 18, 2000.

EXAMPLE 18

5 2.5 Grams of a micronized polyethylene wax (MPP-611, Micro Powders Inc., Tarrytown, New York), was weighed into a crystallizing dish, followed by 1,3-dibromo-5,5-dimethylhydantoin (47.5 g). A broad-bladed spatula was used to blend the mixture rather like a cook might blend butter into flour. After 10 minutes of hand mixing in this fashion, the product was admitted to a glass bottle which was rolled to assess the flowability of the mixture. The flow properties were improved over the properties of the 1,3-dibromo-5,5-dimethylhydantoin used to make the blend.

EXAMPLE 19

10 2.5 Grams of polypropylene wax (MICROPRO 400, Micro Powders Inc., Tarrytown, New York), was weighed into a crystallizing dish, followed by 1,3-dibromo-5,5-dimethylhydantoin (47.5 g). This mixture was blended as described in Example 18, and transferred to a glass bottle which was rolled to assess the flowability of the blend. Its flow properties were improved over the properties of the 1,3-dibromo-5,5-dimethylhydantoin used to make the blend.

EXAMPLE 20

20 The 1,3-dibromo-5,5-dimethylhydantoin blends prepared in Examples 18 and 19 were subjected to a compaction test. Each sample was weighed, and introduced into a 0.71 inch diameter die made from Hastelloy® C alloy and compacted with a screw-driven punch, also made of Hastelloy® C alloy, to a pre-set pressure. Before filling the die, its interior surfaces were lightly dusted with micronized polypropylene wax to serve as a lubricant. There was no
25 dwell time upon attaining the compaction pressure (the pressure was released immediately).

Upon extracting the tablet from the die, the thickness of the tablet was measured with a micrometer, and a visual observation of the tablet was made.

For comparison, the blends were compared to unblended, virgin, commercially produced 1,3-dibromo-5,5-dimethylhydantoin powder with an average particle size of about 64.5 μ , and a commercial toilet bowl product (abbreviated in Table 13 as CTB product), which is known to be a mixture of other halogenated hydantoin compounds. This toilet bowl puck was purchased from a supermarket and ground to a powder with a mortar and pestle, and recompactd as above described.

Table 15 lists the experimental conditions and the observations.

TABLE 15

Blend	Amount of blend added to die	Pressure	Tablet thickness	Observations
DBDMH/5 wt% MPP-611	5.0g	5000 psi	0.389 in.	Intact tablet, smooth shiny surfaces
DBDMH/5 wt% Micropro 400	5.0g	5000 psi	0.374 in.	Intact tablet, not 100% mold release from top punch
DBDMH	2.5g	5000 psi	-	compact shattered and laminated on removal from die
CTB product	2.5g	5000 psi	0.22 in.	Intact tablet

EXAMPLE 21

The 1,3-dibromo-5,5-dimethylhydantoin/5 wt% MPP-611 tablets produced in Example 19 were placed in glass beakers of water. The tablet appeared to do nothing. Its physical integrity remained intact as it slowly dissolved over a period of several months. In order to prove that it was releasing dissolved halogen, the tablet was removed from the water, washed

with deionized water and dried with a paper towel. A plastic wash bottle was then used to wash the tablet into a deionized water solution containing N,N-diethyl-phenylenediamine (DPD) powder. This solution immediately turned pink when the wash water was introduced, proving that soluble halogen was being washed from the tablet. In this connection, DPD is an indicator of high sensitivity used to detect the presence of soluble halogen at the parts per million level. In the presence of such quantities of dissolved halogen, the DPD turns pink.

EXAMPLE 22

1,3-Dibromo-5,5-dimethylhydantoin was blended with micronized polyethylene wax (MPP-611) such that the blend contained 3 wt% of the wax. A sample of the blend (5 g) was introduced to a die made from Hastelloy[®] C alloy, and compacted to a pressure of 5000 psi. Three more samples (5 g each) were compacted in the same manner, and each time a single tablet was extracted from the die after the pressure had been released. In each case, before filling the die, its interior surfaces were lightly dusted with micronized polypropylene wax to serve as a lubricant. The tablets were manually broken into two equally-sized pieces. One half of each tablet was crushed into a powder with a mortar and pestle, and the powder was titrated to determine its wt% of active bromine. The other half of each tablet was placed in a sealed glass vial and placed in an oven at 50 °C. After 30 days, the samples were removed from the oven, ground up, and titrated to determine its wt% of active bromine. For comparative purposes, a control sample of commercially produced 1,3-dibromo-5,5-dimethylhydantoin having an average particle size of about 64.5 μ (containing no micronized polyethylene wax) was subjected to the same operations. In the case of this control sample, it was not possible to extract a single tablet from the die, and thus only shattered laminates could be tested.

Table 16 lists the results obtained for four samples of 1,3-dibromo-5,5-dimethylhydantoin/3 wt% micronized polyethylene wax blends, along with the control sample containing no additive.

TABLE 16

	WT% Active Bromine	
	Initial	After 30 days
Sample 1	53.4	53.3
Sample 2	53.3	53.6
Sample 3	54.2	53.3
Sample 4	53.3	53.7
Control	55.3	55.2

The data in Table 16 indicate that, within the reproducibility of the analytical technique used, the presence of 3 wt% of micronized polyethylene wax in a 1,3-dibromo-5,5-dimethylhydantoin tablet does not induce a loss of active bromine after storage at 50 °C for 30 days. This absence of active bromine loss demonstrates the chemical compatibility of 1,3-dibromo-5,5-dimethylhydantoin and micronized polyethylene wax.

EXAMPLE 23

The strength of 1,3-dibromo-5,5-dimethylhydantoin tableted with different amounts of micronized polyethylene wax, as described in Example 22, was measured in a series of crush strength tests. In each test, 5 g of blended material was added to a die made from Hastelloy[®] C alloy and compressed with a screw-driven punch, also made from Hastelloy C alloy, to a pressure of 5000 psi. In each case, before filling the die, the interior surfaces of the die were lightly dusted with micronized polypropylene wax to serve as a lubricant. After extraction of the tablet from the die, a visual observation of the tablet was made. A Sintech[®] 1/S compression apparatus equipped with Testworks software was used to determine the crush strength of the tablets. This uses a screw-driven piston to exert pressure on the tablet until it breaks. The pressure required to reach the breaking point is recorded and reported as the crush strength.

The crush strength of the tablets was compared to a commercial toilet bowl product (abbreviated as CTB product in Table 17). This was purchased from a supermarket, ground to a powder and re-compacted under the conditions described above.

Table 17 summarizes the observations and results. The crush strength data represent an average of 3 separate measurements.

TABLE 17

Blend	Average thickness	Average crush strength	Observations
DBDMH/5 wt% MPP-611	0.38 in.	93.7 lb./in.*	Single tablets, shiny surfaces, low dust
DBDMH/3 wt% MPP-611	0.38 in.	57.9 lb./in.	Single tablets, shiny surfaces, low dust
DBDMH/2 wt% MPP-611	0.37 in.	37.0 lb./in.	Single tablets, shiny surface, low dust
CTB product	0.44 in.	55.2 lb./in.	Single tablets, dull surfaces, dusty

*An estimate because 2 of the 3 tablets did not break before the limit of the load cell was exceeded.

The data in Table 17 clearly demonstrate that the crush strength of the tablets is a function of the micronized polyethylene wax loading, and that when using micronized polyethylene wax with 1,3-dibromo-5,5-dimethylhydantoin, it is possible to obtain a stronger product than a commercial toilet bowl product.

EXAMPLE 24

A series of different blends was prepared using a variety of micronized waxes (purchased from Micro Powders Incorporated, Tarrytown, New York). Each blend was prepared in the fashion described in Example 18, such that the blend contained 3 wt% wax. The source of the DBDMH used in forming these blends was commercially produced 1,3-dibromo-5,5-dimethylhydantoin having an average particle size of about 64.5 μ . Tableting and crush strength testing were performed as described in Examples 22 and 23.

The crush strength of the tablets was compared to a commercial toilet bowl product (abbreviated as CTB product in Table 18). This commercial toilet bowl product was purchased from a supermarket, ground to a powder, and re-tableted under the conditions described in Example 22.

Table 18 summarizes the observations and results. The crush strength data represent an average of 3 separate measurements.

TABLE 18

DBDMH blend	Average thickness	Average crush strength	Observations
Polyfluo 200 wax	0.38 in.	30.2 lb/in.	Single tablets, tend to end-cap on breaking
Polyfluo 400 wax	0.37 in.	22.2 lb/in.	Single tablets, tend to end-cap on breaking
Micropro 400 wax	0.36 in.	11.8 lb/in.	Single tablets, tend to end-cap on breaking
Synfluo 180 VF	0.38 in.	37.8 lb/in.	Single tablets, tend to end-cap on breaking
Polysilk 600	-	-	Powder is discolored, chemical incompatibility; no tablets were made
Handy Tack 140 resin	0.39 in.	27.5 lb/in.	Tablets are discolored, chemical incompatibility
CTB product	0.44 in.	102.3 lb/in.	Single tablets

Although in the tests summarized in Table 18 the 1,3-dibromo-5,5-dimethylhydantoin tablets were not as strong as the prepared sample of CTB product, nevertheless all of the micronized waxes served as effective binders for 1,3-dibromo-5,5-dimethylhydantoin in that they produced whole tablets that remained intact when extracted from a die, and that exhibited adequate crush strength. However, a micronized modified petroleum resin (Handy Tack 140, Micro Powders Inc., Tarrytown, NY) and a fluorinated hydrocarbon mixture (Polysilk 600,

Micro Powders Inc., Tarrytown, NY) both displayed signs of chemical incompatibility with 1,3-dibromo-5,5-dimethylhydantoin.

EXAMPLE 25

Blending and tableting studies were scaled up. A ribbon blender with a volume of two cubic feet was used to mix 25 kg of commercially produced 1,3-dibromo-5,5-dimethylhydantoin, having an average particle size of about 64.5μ , with micronized polyethylene wax (MPP-611) to achieve loadings of 2.0 wt% and 2.5 wt% of wax. The mixing time was 60 minutes in each case. A double-cone, tumble blender with a volume of 5 cubic feet was used to tumble mix 25 kg of 1,3-dibromo-5,5-dimethylhydantoin with micronized polyethylene wax to achieve a loading of 3 wt% of wax. The mixing time was 240 minutes.

Each blend was passed through a Chilsonator[®] breaker (The Fitzpatrick Company, Elmhurst, Illinois) and a set of screens to produce compacted granules of U.S. mesh size 12 to 18. Virgin, commercially-produced 1,3-dibromo-5,5-dimethylhydantoin having an average particle size of about 64.5μ , without micronized polyethylene wax, was also passed through the same equipment. This material did not compact and form granules. Instead, material exiting the Chilsonator[®] was mostly loose powder.

The granules of each 1,3-dibromo-5,5-dimethylhydantoin/micronized polyethylene wax blend were introduced to the feed hopper of a rotary tablet press. The turret contained 18 die cavities, each of which is 0.75 inches in diameter, which was automatically filled with granules and compressed between two punches made of Hastelloy[®] C alloy. The tablets ejected from the tablet press were collected, and 7 days later were subject to crush strength testing. The results given in Table 19 are an average of at least 3 tests.

TABLE 19

DBDMH Blend	Tablet Thickness	Crush strength
2 wt% MPP-611, tumble blender	0.49 in.	16.6 lb/in
2.5 wt% MPP-611, Ribbon blender	0.49 in.	19.3 lb/in
3 wt% MPP-611, Ribbon blender	0.72 in.	24.1 lb/in

The main findings from the runs of Example 25 were that the commercially produced 1,3-dibromo-5,5-dimethylhydantoin with an average particle size of about 64.5 μ alone cannot be compacted into granules suitable for making tablets, and that the presence of micronized polyethylene wax (MPP-611) with such finely-divided 1,3-dibromo-5,5-dimethylhydantoin promotes the process of compaction into granules. These granules can be fed to a tableting machine and compacted into tablets. The strength of the tablets is governed by the amount of micronized polyethylene wax present. The higher the level of micronized polyethylene wax, the stronger the tablet.

EXAMPLE 26

The crush strength of tablets formed from a large average particle sized 1,3-dibromo-5,5-dimethylhydantoin formulated with a binder was measured. This 1,3-dibromo-5,5-dimethylhydantoin had an average particle size of about 189 microns, and the binder was a micronized polyethylene wax (MPP-611), and the binder was 3 wt% of the blend. The measurements were made utilizing a Sintech 1/S compression apparatus equipped with Testworks software. In these tests the tablets were subjected to increasing force applied along the longitudinal axis of the tablet until breakage occurred. The procedure for producing the tablets was as described in Example 21. The results of the crush strength tests are summarized in Table 20.

TABLE 20

Tablet Thickness	Crush Strength	Crush Strength
0.372 in.	39.8 lb.	107.2 lb./in.
0.375 in.	44.9 lb.	119.9 lb./in.
0.375 in.	37.5 lb.	100.0 lb./in.
0.375 in.	36.1 lb.	96.5 lb./in.
0.377 in.	37.6 lb.	99.7 lb./in.
Averaged Results	39.2 lb.	104.6 lb./in.

As can be seen from the foregoing description, there are a great number of important ways of carrying out or implementing this invention. In brief summary, some of these embodiments are as follows:

5 A) A method of effecting microbiocidal activity in a body of water, which method comprises providing in such body of water using a 1,3-dibromo-5,5-dialkylhydantoin microbiocidal agent described herein (DBDAH), most preferably 1,3-dibromo-5,5-dimethylhydantoin (DBDMH), a concentration of "free chlorine" that is greater than could be predicted from the concentration of "free chlorine" provided by an equimolar amount of N,N'-bromochloro-5,5-dimethylhydantoin (BCDMH), as determinable by comparative testing for "free chlorine" using Hach Method 8021 (copyright 1997, by Hach Company) and for "total chlorine" using Hach Method 8167 (copyright 1997, by Hach Company), and converting the mg/L Cl₂ "free chlorine" values from the tests to percentages of the mg/L Cl₂ "total chlorine" values from the tests, the four water samples used in said tests each having the same pH as said body of water and containing an equimolar quantity of BCDMH or DBDAH.

10 B) A method of A) above wherein the molar amount of the 1,3-dibromo-5,5-dialkylhydantoin microbiocidal agent (DBDAH), most preferably 1,3-dibromo-5,5-dimethylhydantoin, provided in said body of water is less than the molar amount of N,N'-bromochloro-5,5-dimethylhydantoin required to achieve the same degree of microbiological control.

15 C) Individual methods of A) or B) above wherein the 1,3-dibromo-5,5-dialkylhydantoin microbiocidal agent (DBDAH) used is 1,3-dibromo-5,5-dimethylhydantoin having (a) an average particle size in the range of about 20 to about 600 microns, (b) an average particle size of at least about 175 microns, (c) an average particle size of at least about 200 microns, (d) an average particle size of at least about 300 microns, or (e) an average particle size of at least about 400 microns.

20 D) Individual methods of A) or B) above wherein the 1,3-dibromo-5,5-dialkylhydantoin

microbiocidal agent (DBDAH) used is (i) 1,3-dibromo-5,5-dimethylhydantoin in the form of a compacted product produced without a binder, or (ii) at least one 1,3-dibromo-5,5-dialkylhydantoin microbiocidal agent described herein (DBDAH), most preferably 1,3-dibromo-5,5-dimethylhydantoin, in the form of a compacted product produced using as a binder an amount of a micronized synthetic polyolefin-based hydrocarbon wax and/or a micronized synthetic polyfluorocarbon wax effective to form the compacted product, the wax being compatible with the 1,3-dibromo-5,5-dialkylhydantoin, or (iii) is in the form of a compacted product formed from at least one 1,3-dibromo-5,5-dialkylhydantoin microbiocidal agent described herein (DBDAH), most preferably 1,3-dibromo-5,5-dimethylhydantoin, wherein the compacted product was produced using as a binder an amount of a saturated, normally solid, fatty amide effective to form the compacted product.

E) Individual methods of (i) of D) above wherein the 1,3-dibromo-5,5-dimethylhydantoin being used has an average particle size of at least about 175, at least about 200, at least about 300, or at least about 400, microns.

F) Individual methods of (ii) of D) above wherein the wax is micronized polyethylene wax having, prior to compaction, an average particle size of no greater than about 15 microns, a maximum particle size of no greater than about 40 microns, and a density in the range of about 0.9 to about 1.4 grams per cc at 25°C; or a micronized polyethylene wax that, prior to compaction, melts at a temperature in the range of about 109°C to about 111°C; or a micronized polypropylene wax having, prior to compaction, an average particle size in the range of about 5.0 to about 7.0 microns, a maximum particle size of about 22 microns, and a density in the range of about 0.9 to about 1.4 grams per cc at 25°C; a micronized polypropylene wax that melts at a temperature in the range of about 140°C to about 143°C, that has an average particle size in the range of about 5.0 to about 7.0 microns, and that has a maximum particle size of about 22 microns.

G) Individual methods of (iii) of D) above wherein the 1,3-dibromo-5,5-dialkylhydantoin being used is 1,3-dibromo-5,5-dimethylhydantoin having an average particle size of at least about 200, at least about 300, at least about 400, or at least about 500, microns.

H) Individual methods of A) or B) above wherein the microbiocidal activity in said body of water comprises combating *Escherichia coli* and/or *Enterococcus faecium* in said body of water.

I) A method of purveying a microbiological control agent for use in water in accordance with U. S. Environmental Protection Agency regulations, which method comprises purveying a container of a water control agent comprising at least one 1,3-dibromo-5,5-dialkylhydantoin microbiocidal agent described herein (DBDAH), most preferably 1,3-dibromo-5,5-dimethylhydantoin, the container bearing a label having thereon dosage levels and indicating either on said label, or on or in packaging for said container, to the effect that the contents are recommended for use, or are for use, in water treatment.

J) Individual methods of H) or I) above wherein the 1,3-dibromo-5,5-dialkylhydantoin being used in H) or the control agent being used in I) is (i) 1,3-dibromo-5,5-dimethylhydantoin in the form of a compacted product produced without a binder, (ii) at least one 1,3-dibromo-5,5-dialkylhydantoin microbiocidal agent described herein (DBDAH), most preferably 1,3-dibromo-5,5-dimethylhydantoin, in the form of a compacted product produced using as a binder an amount of a micronized synthetic polyolefin-based hydrocarbon wax and/or a micronized synthetic polyfluorocarbon wax effective to form the compacted product, the wax being compatible with the 1,3-dibromo-5,5-dialkylhydantoin, or (iii) at least one 1,3-dibromo-5,5-dialkylhydantoin microbiocidal agent described herein (DBDAH), most preferably 1,3-dibromo-5,5-dimethylhydantoin, in the form of a compacted product formed from the 1,3-dibromo-5,5-dialkylhydantoin wherein the compacted product was produced

using as a binder an amount of a saturated, normally solid, fatty amide effective to form the compacted product.

5 K) Individual methods of (i) of J) above wherein the 1,3-dibromo-5,5-dimethylhydantoin being used has an average particle size of at least about 175, at least about 200, at least about 300, or at least about 400, microns.

10 L) Individual methods of (ii) of J) above wherein the wax is polyethylene wax having, prior to compaction, an average particle size of no greater than about 15 microns, a maximum particle size of no greater than about 40 microns, and a density in the range of about 0.9 to about 1.4 grams per cc at 25 °C; or wherein the wax is a polyethylene wax that, prior to compaction, melts at a temperature in the range of about 109 °C to about 111 °C; or wherein the wax is polypropylene wax having, prior to compaction, an average particle size in the range of about 5.0 to about 7.0 microns, a maximum particle size of about 22 microns, and a density in the range of about 0.9 to about 1.4 grams per cc at 25 °C; or wherein the wax, prior to compaction, is a polypropylene wax that melts at a temperature in the range of about 140 °C to about 143 °C, that has an average particle size in the range of about 5.0 to about 7.0 microns, and that has a maximum particle size of about 22 microns.

15 M) Individual methods of (iii) of J) above wherein the 1,3-dibromo-5,5-dialkylhydantoin used in forming the compacted product is 1,3-dibromo-5,5-dimethylhydantoin having an average particle size of at least about 200, at least about 300, or at least about 400, microns.

20 N) Individual methods of any of A)-M) above wherein the body of water being treated is industrial cooling water, wastewater, or process water.

O) A method of N) above wherein the treatment of the water comprises passing a sidestream of the water through a bed of the 1,3-dibromo-5,5-dialkylhydantoin such that a biocidally effective amount of the 1,3-dibromo-5,5-dialkylhydantoin is delivered to the water.

P) Individual methods of I) above wherein the microbiological control agent is purveyed for use in at least cooling water, wastewater, or process water.

Q) Individual methods of A) or B) above wherein the microbiocidal activity in said body of water comprises eradicating, substantially eradicating, or reducing biofilm on a surface in contact with said body of water.

R) Individual methods of Q) above wherein the 1,3-dibromo-5,5-dialkylhydantoin being used is 1,3-dibromo-5,5-dimethylhydantoin having (a) an average particle size in the range of about 20 to about 600 microns, (b) an average particle size of at least about 175 microns, (c) an average particle size of at least about 200 microns, (d) an average particle size of at least about 300 microns, or (e) an average particle size of at least about 400 microns.

S) Individual methods of Q) above wherein the 1,3-dibromo-5,5-dialkylhydantoin being used is (i) 1,3-dibromo-5,5-dimethylhydantoin in the form of a compacted product produced without a binder, or (ii) at least one 1,3-dibromo-5,5-dialkylhydantoin described herein (DBDAH), most preferably 1,3-dibromo-5,5-dimethylhydantoin, in the form of a compacted product produced using as a binder an amount of a micronized synthetic polyolefin-based hydrocarbon wax and/or a micronized synthetic polyfluorocarbon wax effective to form the compacted product, the wax being compatible with the 1,3-dibromo-5,5-dialkylhydantoin, or (iii) at least one 1,3-dibromo-5,5-dialkylhydantoin described herein (DBDAH), most preferably 1,3-dibromo-5,5-dimethylhydantoin, in the form of a compacted product formed from the 1,3-dibromo-5,5-dialkylhydantoin wherein the compacted product was produced using as a binder an amount of a saturated, normally solid, fatty amide effective to form the compacted product.

T) Individual methods of (i) of S) above wherein the 1,3-dibromo-5,5-dimethylhydantoin being used has an average particle size of at least about 175, at least about 200, at least about 300, or at least about 400, microns.

U) Individual methods of (ii) of S) above wherein the wax is micronized polyethylene wax having, prior to compaction, an average particle size of no greater than about 15 microns, a maximum particle size of no greater than about 40 microns, and a density in the range of about 0.9 to about 1.4 grams per cc at 25°C; or a micronized polyethylene wax that, prior to compaction, melts at a temperature in the range of about 109°C to about 111°C; or a micronized polypropylene wax having, prior to compaction, an average particle size in the range of about 5.0 to about 7.0 microns, a maximum particle size of about 22 microns, and a density in the range of about 0.9 to about 1.4 grams per cc at 25°C; a micronized polypropylene wax that melts at a temperature in the range of about 140°C to about 143°C, that has an average particle size in the range of about 5.0 to about 7.0 microns, and that has a maximum particle size of about 22 microns.

V) Individual methods of (iii) of S) above wherein the 1,3-dibromo-5,5-dialkylhydantoin being used is 1,3-dibromo-5,5-dimethylhydantoin having an average particle size of at least about 200, at least about 300, at least about 400, or at least about 500, microns.

W) Individual methods of A) or B) above wherein the microbiocidal activity in said body of water comprises eradicating, substantially eradicating, or at least reducing *Pseudomonas aeruginosa* biofilm on a surface in contact with said body of water.

X) A method of purveying a biofilm control agent for use in water in accordance with U. S. Environmental Protection Agency regulations, which method comprises purveying a container of a biofilm control agent for use in aqueous media, such agent comprising at least one 1,3-dibromo-5,5-dialkylhydantoin described herein (DBDAH), most preferably 1,3-

dibromo-5,5-dimethylhydantoin, the container bearing a label having thereon dosage levels and indicating either on said label, or on or in packaging for said container, to the effect that the contents are recommended for use, or are for use, in water.

References herein to biofilm on a surface in contact with an aqueous medium or water, are not to be construed as requiring the aqueous medium or water to be in constant contact with such surface. As long as the aqueous medium or water comes into contact with a surface often enough to result in the formation of biofilm on such surface, it is within the scope of this invention to treat such aqueous medium or water pursuant to this invention so as to combat such biofilm. For example, this invention includes treatment of aqueous media or water that is splashed, sprayed, or dripped on or against a surface with sufficient frequency for biofilm to develop on such surface. It is also to be understood that the aqueous medium or the water can contain any of a variety of contaminants and/or impurities. The only requirements are that such aqueous medium or water periodically or constantly contacts a surface such that the formation of biofilm occurs on the surface, and that the contaminants and/or impurities in the aqueous medium or water do not prevent the 1,3-dibromo-5,5-dialkylhydantoin(s) such as 1,3-dibromo-5,5-dimethylhydantoin, from eradicating, or at least reducing the amount of, the biofilm on such surface.

As used herein, including the claims, the term "purveying" means carrying out or causing to be carried out one or more of the following activities: advertising, marketing, promoting for sale, offering for sale, selling, bartering, trading, leasing, merchandising, importing, exporting, dealing in commerce with, supplying, distributing, delivering, and any and all other activities of similar import.

As used herein, including the claims, the terms "aqueous medium" and "water" refer to and include any liquid in which the predominate liquid component is water. Such aqueous medium or water may contain various other materials, whether organic or inorganic, or both,

and is exemplified by recreational water, industrial cooling water, process water and wastewater. As is well known in the art, if the water has a pH of at least about 8, it is not included in the category of recreational water, at least at the present time in the United States.

5 Compounds referred to by chemical name or formula anywhere in this document, whether referred to in the singular or plural, are identified as they exist prior to coming into contact with another substance referred to by chemical name or chemical type (*e.g.*, another component, a solvent, or *etc.*). It matters not what preliminary chemical changes, if any, take place in the resulting mixture or solution, as such changes are the natural result of bringing the specified substances together under the conditions called for pursuant to this disclosure. Also, even though the claims may refer to substances in the present tense (*e.g.*, "comprises", "is", *etc.*), the reference is to the substance as it exists at the time just before it is first contacted, blended or mixed with one or more other substances in accordance with the present disclosure.

10 Except as may be expressly otherwise indicated, the article "a" or "an" if and as used herein is not intended to limit, and should not be construed as limiting, a claim to a single element to which the article refers. Rather, the article "a" or "an" if and as used herein is intended to cover one or more such elements, unless the text expressly indicates otherwise.

15 It will also be understood that the terms "substantial" and "substantially" denote that chemical operations or treatments ordinarily do not involve absolutes. Thus instead of describing a variable or a result as an absolute, it is far more realistic to describe the variable or result as being in the substantial vicinity of the expressed variable or result. For example
20 when describing eradication of an organism, it can be more realistic to refer to the substantial eradication of the organism rather than to imply that absolute total eradication occurs, since one skilled in the art fully realizes that a substantial kill is a very desirable result, and the
25 possibility always exists that even if a small portion of the organism survives the treatment,

the overall result is nevertheless highly beneficial in most cases. Thus this document should be read with the application of reason and common sense.

As used herein the term "water-soluble" means that the biocidally-active ingredient in question has at least sufficient solubility to provide adequate biological control in the water in which it is used. The ingredient may still have greater solubility but need not be soluble in all proportions in water.

As used herein the term "sticker" means any label which can be affixed by any method to packaging material such that the contents of the sticker can be perceived visually from the exterior of the package.

Each and every patent, publication, or commonly-owned patent application referred to in any portion of this specification is incorporated *in toto* into this disclosure by reference, as if fully set forth herein.

This invention is susceptible to considerable variation in its practice. Therefore the foregoing description is not intended to limit, and should not be construed as limiting, the invention to the particular exemplifications presented hereinabove. Rather, what is intended to be covered is as set forth in the ensuing claims and the equivalents thereof permitted as a matter of law.